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CHEMISTRY IN COMMERCE

A COMPREHENSIVE, PRACTICAL AND AUTHORITATIVE
GUIDE, SHOWING HOW CHEMICAL PRINCIPLES ARE
APPLIED IN ACTUAL PRACTICE

Advisory Editor

M. D. CURWEN, B.Sc., A.I.C.

VOLUME IV

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*Index and Classified Key which enable
references to any subject to be
readily found are given at the end
of this volume*

BACTERIOLOGICAL EXAMINATION OF WATER

PART I.—THE HISTORY OF BACTERIOLOGICAL RESEARCH

By H. F. FERMOR, F.I.C.

PUBLIC usefulness and the interests of humanity ennoble the most disgusting work and only allow enlightened men to see the zeal which is needed to overcome obstacles." Lavoisier

Such was considered to be the truth, so far as manufacturing chemistry was concerned, at the time of the French Revolution. A history of the subject would show it to be a much broader truth in the case of bacteriology, for in the examination of a sample of water the object is to detect sewage pollution and organisms which give rise to such diseases as cholera and typhoid fever.

In considering the purity of a water supply it was for long considered that the analyst could give a speedy and definite opinion. Such an idea is no longer tenable because it is now known that the aid of the physicist, the geologist and the biologist is also needed

the specific gravity of various kinds of water; he showed how nitrate of silver would detect one grain of salt in a thousand of water; he employed ammonia for the detection of copper; used extract of galls to ascertain the presence

of iron, and in syrup of violets found a reagent which indicated acidity or alkalinity in water.

Kircher.

All these tests were physical or chemical, but a few years later Athanasius Kircher, a learned Jesuit suggested that some diseases were due to a "contagium animatum," or living cause, as in his investigation upon the microscopy of putrid meat he had observed "minute living worms."

Dr. Graaf.

On 28th April, 1673, Dr. Graaf, a foreign correspondent of the newly formed Royal Society of

London, wrote to the secretary Oldenburg that "one Mr. Leuwenhoeck hath lately contrived microscopes excelling those that have hitherto been made."

Leuwenhoeck's Experiments.

Anthony van Leuwenhoeck lived at a time when authority, while dominant, was beginning to fade, when the ideas of



Fig. 1.—ROBERT BOYLE
Who in 1663 described various tests which could be applied to ascertain the purity of a sample of water

Boyle's Tests.

Robert Boyle in a paper on "Experiments Touching Colours," written in 1663, showed how various tests could be applied to ascertain the purity of a sample of water. He published the earliest table of

Francis Bacon as to the advantages of experiment were being tested, when prominent men in the scientific world devised ingenious apparatus on week days and preached long and prosy sermons on Sundays which afforded opportunities for men like Dean Swift in after years to write "Meditations on a Broomstick."

As men are measured at the present day, Leuwenhoeck would be classed as a man of little learning. He knew only his native tongue and read that from a Dutch Bible. The scientific men of the period corresponded and spoke in the Latin tongue. Nevertheless he had educated himself, and his ignorance of current learning caused him to trust his own eyes, his own thoughts, and his own judgment, even if he did consume time doing things for himself, for he spoke the truth when he said:

"People who look for the first time through a microscope say now I see this, then I see that, and even a skilled observer can be fooled. On these observations I have spent more time than many will believe, but I have done it with joy and I have taken no notice of those who have said 'Why take so much trouble and what is the good of it?' But I do not write for such people, but only for the philosophical."

Pepper Water—The First Culture Medium.

One day, in examining through one of his microscopes a sample of water from a rough rain gauge in his garden, he saw some little animals "a thousand times smaller than the eye of a large louse."

He was looking at what the nineteenth century microscopist called animalculæ. As was befitting a man of the period, he very frequently asked himself questions and then tried to answer them, not from his inner consciousness but by making an appeal to experiment.

"Why," said he, "does pepper taste hot? There must be little points on the particles of pepper which irritate the surface of the tongue when pepper is eaten."

But pepper is hard and his difficulty was to powder it finely enough to see if the points were there, so he soaked the pepper in water and then, taking some of the infusion, looked for the fine points. These he failed to find but in the water he did see "an incredible number of little animals of various sorts which move very prettily, which tumble about and sideways this way and that." He calculated that there would be about 2,700,000 "in a large grain of sand."

In the pepper water he had discovered what the moderns would call a culture medium.

The Fellows of the Royal Society were somewhat

surprised on receiving this communication, so they appointed a small committee consisting of two of their number, Robert Hooke and Dr. Nehemiah Grew, to investigate the matter and to report thereon. Accordingly some of the best black pepper was purchased, an infusion of the same made and the best microscope of the Society brought into use and on the 15th November, 1677, the committee members gave a demonstration before as



Fig. 2.—LOUIS PASTEUR.

Who found that by inoculating animals with increasing doses of a dangerous microbe they became immune and that their blood serum conferred immunity upon other animals.

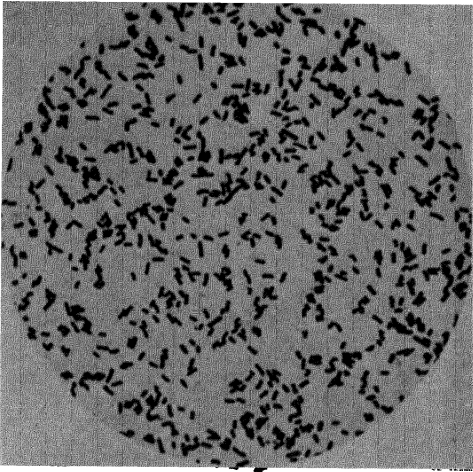


Fig 3 —TYPICAL MICROBES OF *B. TYPHOSUS*
($\times 900$).

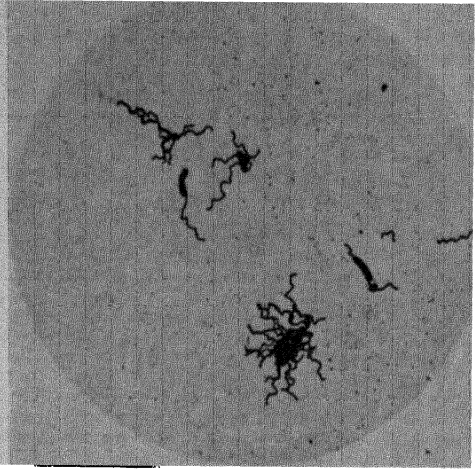


Fig 4 —TYPICAL MICROBES OF *B. TYPHOSUS*
($\times 1,000$), SHOWING FLAGELLIA

many of the Fellows who could find time to be present—and they saw the small animals swimming about in the liquid.

These little animals seemed to be ubiquitous for, as Leuwenhoeck observed, he saw swarms of them when he examined material he obtained upon those somewhat rare occasions when he was “troubled with a looseness.” In fact, he was looking at, amongst other things, specimens of the *Bacterium Coli Communis*, the microbe which is now used as an index of the pollution of potable water.

Leuwenhoeck's Discovery of Microbes in the Human Mouth.

On another occasion, in 1683, he writes to the Society, “Although I am fifty years old I have uncommonly well-preserved teeth but . . . I saw with great astonishment, especially in the material mentioned (an emulsion of the tartar from between the teeth) that there were many tiny animals which moved about in a most amusing manner, the largest of these showed the liveliest and most active motion, moving through water or saliva as a fish of prey darts through the sea ,

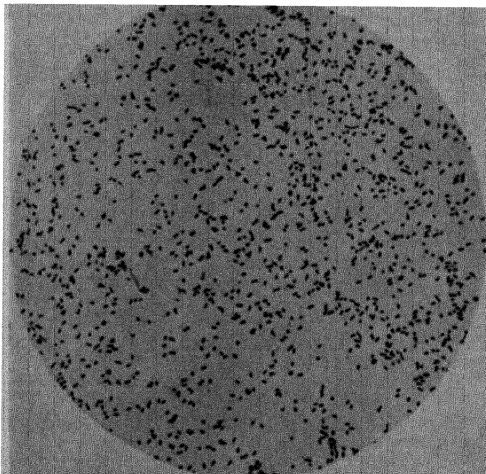


Fig 5 TYPICAL MICROBES OF *B. COLI COMMUNIS* ($\times 500$)

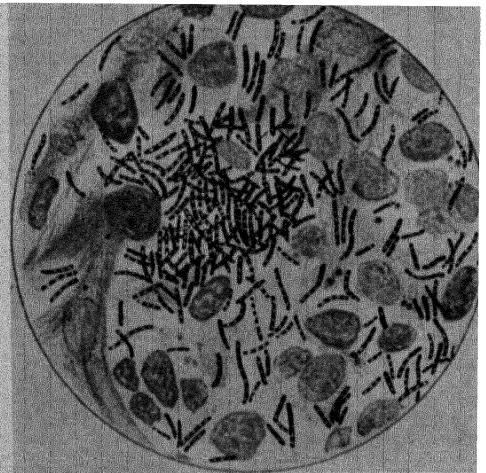


Fig 6 TYPICAL MICROBES OF *B. TUBERCULOSIS*.

they were found everywhere although not in large numbers."

Leuwenhoeck had discovered microbes in the human mouth. He had very human characteristics and in continuing his letter he writes, "When I have supped too heavily of an evening, I drink, in the morning, a large number of cups of coffee and that as hot as I can drink it, so that a sweat breaks out on me."

On testing the tartar from his front teeth after such a performance he discovered that the little animals were still there but not moving and apparently dead. The tartar from his back teeth contained the living microbes as usual. Coffee or heat, probably the latter, had killed the micro-organisms in his front teeth. In modern language it could be said that he had found out how to sterilize things, in this case teeth, by the application of heat.

Leuwenhoeck was an investigator in a new field, an accurate and conscientious observer, an honest man, with common sense above the average but, according to the standards of the time, uneducated.

Spallanzani and Spontaneous Generation.

Six years after the death of Leuwenhoeck there was born at Scandiano in Northern Italy a boy who was christened Lazzaro Spallanzani. He was educated for the law but was much more interested in literature and mathematics. He eventually became a priest in the Roman Catholic Church when he found time to carry out scientific experiments and very early in his career he became interested in one of the burning questions of the day: Is there such a phenomenon as spontaneous generation?

The ideas of the scientists of the time on the subject we should now describe as quaint. To procure a swarm of bees, for example, all that was necessary was to kill a young bullock and bury his corpse in a standing position with his horns above the ground. He was left in this condition for a month and at the end of the period,

at the waxing of the moon, his horns were sawn off, and out flew a swarm of bees.

Spallanzani investigated small living creatures. He showed that these obeyed the laws of Nature, that they were present everywhere, that they could not survive at the temperature of boiling water for an hour and that some could grow in an atmosphere free from oxygen. He had a correspondence with de Saussure as to whether microbes multiplied by division and proved that such was the case by noting the action of one micro-organism in water. He saw it become gradually thinner at the middle and then, with a little jerk become two individuals.

This experiment and the fact that in investigating the habits of small living things it was necessary in the first place to use apparatus free from microbes, that

is, sterile, led to the conclusion that spontaneous generation was impossible, although the fact was not satisfactorily demonstrated until the time of Pasteur and Tyndall when the problem was regarded

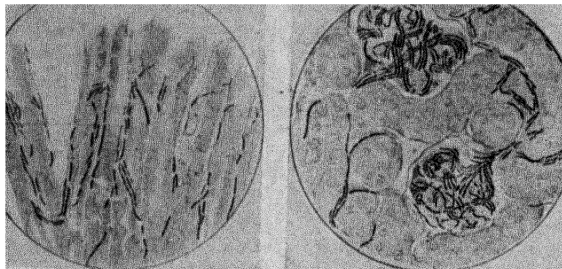
as one in relation to the theological controversies of the time rather than one concerning science.

It has been shown that a draper of Delft and an Italian priest investigated the life histories of small living creatures. One could hardly call them plants and yet did not like to class them as animals.

Louis Pasteur.

The next important step in the study of these unicellular organisms was taken by a chemist, Louis Pasteur. His work in connection with the Fermentation Industries has been described elsewhere.

Up to 1879 Pasteur was regarded as a chemist; for the rest of his life he was looked upon as a medical man. His work was now to be in the direction of curing humanity afflicted with some of the diseases due to micro-organisms.



Puerperal Fever.

First he studied puerperal fever which he said was carried from one patient to another by medical attendants and was due to a "*micrococcus sous forme de chapelets*." This was in 1879. Next Pasteur said that the spread of anthrax, more particularly in sheep, was due to earthworms carrying the specific organisms which gave rise to the disease from buried animals to the surface of the pastures.

Inoculation of Animals.

By inoculating animals with increasing doses of a dangerous microbe, such as anthrax, he found that they became immune and their blood serum conferred immunity upon other animals. Certain pathogenic bacteria can produce poisons which dissolve in liquid nutrient media and are known as true bacterial toxins. They are produced typically by the organisms which give rise to the diseases of diphtheria and tetanus. If an animal be given a mild attack of a disease, changes occur in its blood stream leading to the formation of a substance which tends to neutralise the effects of the toxin present so that the animal recovers from the disease and it becomes immune. This is due to the presence of an antitoxin.

Vaccination.

Pasteur adopted the method of vaccination. That is he made a culture of the organisms he required to a temperature of 42.5° for 24 days. At the end of this period the bacteria were dead but the products of their metabolism remained, one of these being an antitoxin in solution which was available for inoculations. Pasteur had discovered a new vaccine and it was a body of this nature which he made, aided by his assistants Roux, Chamberland and Thuillier, to

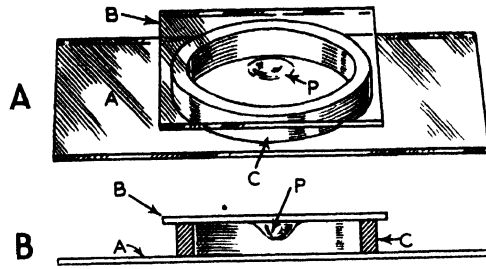


Fig 8.—SUSPENDED DROP-CULTURES (A) A, glass slide, B, cover-glass, C, glass ring forming the wall of the chamber, P, drop of nutritive liquid in which the micro-organisms grow (Klein) (B), side view of above

cure the dread disease hydrophobia, the first case to be so treated being the boy Meister on the night of 6th July, 1885, and he made a good recovery.

Ten years later Pasteur died. An old man to whom scientists paid tribute, the best known man in France, possibly in

Europe, and in the Institute Pasteur at Paris, where his work is still carried on, can be seen his most enduring monument.

Koch's Study of the Microbe.

Robert Koch was one of the pioneers in the study of the microbe as a cause of disease. While others thought, he proved. He graduated from a German medical college in 1866, obtained an appointment as medical officer in an asylum and eventually became a general practitioner.

His mode of life and his whole outlook on the universe was changed when on his 28th birthday his wife gave him a microscope. Perhaps she thought it would make him have a more contented mind and keep him more at home in the evenings. It did and as soon as he found out how to use it he delved into the unknown. It was not long before he isolated the micro-organism which gave rise to anthrax in sheep and wool-sorters' disease in men.

The "Hanging Drop" Method of Obtaining Pure Cultures.

Living, as he did, in a thinly populated neighbourhood remote from cities, he had to devise his own methods of research and to invent most of his own apparatus, one of the earliest and most useful being the "hanging drop" for obtaining pure cultures. It consists of a drop of culture hanging from a cover-slip.

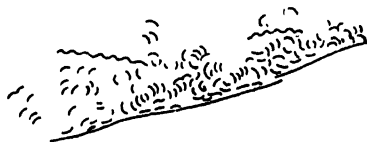


Fig 9 —TYPICAL MICROBES OF CHOLERA

culture and note the morphology and behaviour of the living microbe, he could make sub-cultures of the microbe into various media or inject some of the organisms into animals and note the result and thus show that a certain disease is due to a specific micro-organism.

Anthrax.

Then he discovered that the bacillus of anthrax had spores which, under suitable conditions, developed into bacilli, and by 1876 he had definitely shown that these were the cause of a disease.

Next he stained dead bacilli with various dyes in order to render them more easily visible when viewed under the microscope. This procedure, in the hands of such men as Loeffler, Ehrlich and others, became a means of identification and differentiation.

Then he took photographs of the micro-organisms and so eliminated, to some extent, the personal factor and obtained more or less permanent records as to their size and shape.

The First Solid Medium.

Hitherto the microbes were cultivated in a liquid medium which possessed obvious disadvantages, but one day Koch saw a piece of neglected boiled potato on which was growing some moulds. This gave him an idea and he tried to cultivate microbes on a diet of boiled potato. To his astonishment he was successful. He had discovered a solid medium and a new method of obtaining pure cultures, so he and his assistants, Loeffler and Gaffky, carried on the work. The advantages of a solid medium for the cultivation of microbes was soon acknowledged and gelatine and agar were added to the list.

Tuberculosis.

On 24th March, 1882, was published one of the greatest discoveries of Koch, for, on that date, he announced that he had found the cause of tuberculosis. It had been isolated on a blood serum.

Asiatic cholera
called comma
bacteria, Fehleisen
typhoid and boils
micro-organisms,

frequently growing in the form of chains and now called streptococci.

To Koch we owe the proof that some diseases are due to specific micro-organisms, the use of solid media, and the preparation of pure cultures. When Koch died, the study of bacteriology had risen from the empiricism of Leuwenhoeck to the logical methods of Pasteur and Koch, so that it was nearer to becoming a branch of scientific study than ever been before.

No one doubts at the present day that the analytical chemist can detect minute quantities of some dangerous substances, but in the examination of water the microbe eluded him and he unwittingly passed as pure, samples of water which were by no means above suspicion on other grounds.

Then came the opportunity for the bacteriologist. Acting on the maxim "Slow but sure," he showed that if the microbes were allowed to grow and live their lives they could not be treated as "organic matter" in chemical apparatus. Results could be obtained by the bacteriologist which were really useful and could not be ignored. Provide the reagents, a suitable environment, and the microbe will, in due course, reveal its identity.

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methods used for the examination of
water for bacteria.

THE CHEMICAL CONTROL OF BREADMAKING

By F. E. THOMAS, M.A. (Oxon), A.I.C.

THE fundamental raw materials of the baker are flour, water, yeast and salt. To these should be added a fifth which, though it does not deserve the title "fundamental," is becoming practically a necessity in present-day conditions. We may term this fifth ingredient by the wide name of "baking aids."

Forms of "Baking Aids."

It may take many forms, such as fat or oil, for enriching purposes, malt flour or extract, traditionally added as flavour improvers and now realised to be essential in certain flours low in diastase, e.g., Australian and Plate, and milk powder, or an "improver" or "yeast food," which may be of the "chemical" kind, consisting of certain harmless mineral salts which feed and assist the action of the yeast and affect the gluten, as described later, or the "non-chemical" kind, consisting of such old-fashioned materials as scalded flour and the like, still occasionally used. Two or more of these can be used in combination.

Proportions of Materials Used.

The first step in the process consists in making as uniform a mixture as possible of the various ingredients. The actual proportions of the materials used depend on the kind of bread it is proposed to make, e.g., cottage or tin bread, etc., the locality in which the bakery is placed, i.e., Scotland requires a different type of bread from

Lancashire; Lancashire bread would not be popular in Birmingham, and none of the three would sell well in, say, London or South Wales; the process to which it is to be subjected, i.e., a short process of 2-3 hours, a longer one of 4-6 hours or the method known as the sponge and dough, in which part of the ingredients are

allowed to ferment for a certain time before the dough is completed by the addition of the remainder of the ingredients.

The variations in process adopted are very numerous, even in the same town, supplying the same type of palate, bread will be made in several different ways, according to the ideas of the individual master baker. The varia-

tions in the quantities used and in the kinds of bread marketed are not, however, very great as a rule.

Preparation of the Dough.

The dough is made in a kneader of which there are many types. The flour is put into the bowl of the kneading machine and its temperature taken. The doughmaker requires his finished dough to be at a certain temperature and from the temperature of the flour he can either calculate or read off on prepared tables the temperature at which he should take the water.

This latter is contained in a "tempering" tank which is fitted with a thermometer and marked off in gallons and fractions thereof, and fitted with a hot and cold water supply. A small quantity



Fig. 1—THE GLUTEN TEST (1).
A small dough is squeezed in the palm of the hand under water until the protein mass (gluten) is freed from starch

of water is drawn off and the remainder run on to the flour. The yeast is made into a suspension with part of the water, and malt flour and extract can be conveniently added to the vessel containing the yeast. This is then added to the flour and water.

Adding the Salt.

The salt (and chemical improver if used is best dissolved in another portion of water, though it is frequently added dry and) in most cases, dissolves before the dough becomes too stiff. In no case must it be dissolved in the same water as the yeast.

Fat and milk powder, if used, should preferably be added in an emulsified state, though there is still considerable divergence of opinion as to whether the extra trouble occasioned by emulsifying is worth the while. The kneader is then started and the dough made in 10-15 minutes.

In up-to-date bakeries, the pans can be removed from the machine and the doughs retained in them, covered with a cloth to prevent skinning and to keep them clean. If of the immovable type, the dough must be lifted out and placed in troughs. The bowls or troughs are placed in a part of the bakery free from draughts and allowed to stand for a period previously determined.

Changes in the Dough.

What actually happens in the dough during this fermentation period? This is only very incompletely understood. The main changes are the development of gas to aerate and lighten the dough and the "maturing" of the gluten, resulting in a well-risen loaf of good texture. This development of gas continues in the dough right up to the oven and is largely a pure waste of material in the early stages. The

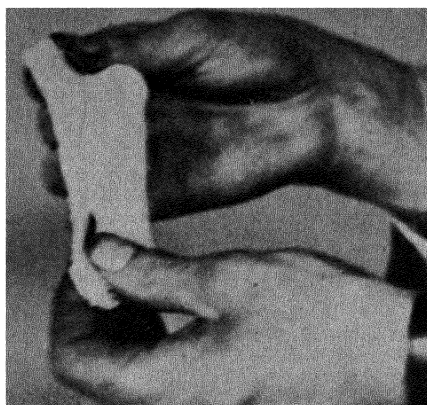


Fig. 2. THE GLUTEN TEST (2).

Deductions can be drawn from the elasticity and extensibility of the gluten, as to the suitability of the flour for any particular baking process.

broad lines of the mechanism of these changes are fairly intelligible.

An Extremely Complex Mixture.

Dough, however, is an extremely complex mixture. To begin with, flour itself has never been completely analysed into 100 per cent. of its constituent substances. Its main constituents are: water, gluten, fat, carbohydrates and ash. The gluten consists of proteins and we do not know *all* the proteins that are

present. The carbohydrates are mainly starch and the chemistry of starch is still in an unsolved state.

We start, therefore, with an incompletely known quantity as our main ingredient, to which we add—in the first place, salt and water. Now all natural waters contain in solution certain mineral salts. Some of these latter salts, those of calcium and magnesium and ordinary common salt, have a very appreciable action on gluten in particular. Flour when doughed up with salt and water forms, as we have stated, a colloid complex. We have present also in dough various enzymes derived from yeast and from the flour itself, which find themselves in a medium more or less favourable to activity.

Bacteria.

There are bacteria in flour and it is moreover, impossible to exclude bacteria present in the air and during a long fermentation numerous by-products may be formed, which are extremely likely to have a definite influence on the flavour and other characteristics of the loaf.

The Fermentation.

Meanwhile, the dough has been fermenting. The yeast will have acted on the sugars present in the flour and produced from the starch of the flour carbon dioxide and alcohol. The change is not a simple one and does not take place in

one stage. Secondary reactions take place and numerous bodies have been identified in small quantities in dough. The carbon dioxide produced renders the dough acid and aerates it, the small bubbles permeate its mass, making the network which is characteristic of a cut loaf.

Without aeration, bread would be an extremely heavy and unpleasant food to eat and difficult to digest. More carbon dioxide is produced, however, than is necessary merely to aerate the dough and inasmuch as all the carbon dioxide and alcohol produced come from the flour and therefore represent so much flour solids, and are subsequently expelled into the air, thus being entirely lost as food, it is clear that the reasons for a longer fermentation than is necessary for aeration alone must be good ones.

"Maturing" of the Dough.

This second object is the "maturing" of the dough, and is the main object of fermentation. Aeration can be achieved by other methods, e.g., baking powders or forcing air into the dough, as was actually done on the commercial scale at one time. A comparison of the flavour of yeast-raised and baking-powder-raised loaves shows that yeast fermentation accomplishes a good deal more than mere aeration. The end aimed at is the modification of the gluten—that portion of the dough which forms the network and constitutes the skeleton of the loaf—in such a way that it will be extensible and at the same time strong enough both to retain the gas in the oven and to expand, giving a light loaf without unseemly tears.

While all the factors affecting this maturing are not known, the important ones are recognised and the chief one is the hydrogen-ion concentration of the dough. As mentioned above, the dough is rendered acid by the carbon-dioxide present,

and this affects the maturing very favourably.

The Proteolytic Enzymes.

Another influence at work in long doughs is the proteolytic enzymes, which have the power of breaking up complicated proteins such as glutenin and gliadin, of which gluten is mainly composed, down to less complex proteins. This process of degradation must not proceed too far, otherwise the gluten will lose its character too definitely, nor, equally, must the acids be allowed to act excessively on the dough, otherwise the dough will be "over" fermented and will make bread of a squat, heavy and unappetising appearance.

Effect of Mineral Salts on Gluten Maturing.

It has also been found that certain mineral salts have an accelerating action as regards gluten maturing, so that instead of allowing 2-3 hours for the formation of these acids and for their action and that of the enzymes in the gluten to take place, the time can be reduced by 20 per cent and more. Inasmuch as, during all this time, yeast is at the same time destroying flour solids and producing carbon dioxide and alcohol from them, it can be seen that the use of these maturing agents results in an appreciable saving of flour, with a resultant greater yield of bread from the sack of flour.

"Cutting Back" the Dough.

Should the fermentation period be over two hours, it is a common and beneficial practice to "cut back" the dough. This process consists in turning over and squeezing the dough so as to reduce its volume. The accumulation of alcohol in the interior of a big mass of dough tends to kill the yeast and by turning it over in this way, a certain amount of the alcohol is driven off, fresh surfaces are



Fig. 3 —THE GLUTEN TEST (3)

After excess water has been squeezed out of the gluten, it is stretched on a filter paper and weighed. It is dried at 100° C and a wet weight-dry weight ratio affords useful information.

exposed to the air, a certain amount of air occluded in the dough, and parts of the dough which may not have been in contact with the yeast have a chance of being acted upon. The actual time or times when this cutting back is carried out vary according to the length of the process and the idiosyncracies of the master baker, but in a four-hour process would normally be after $2\frac{1}{4}$ and either $3\frac{1}{4}$ or $3\frac{1}{2}$ hours.

After-fermentation Treatment.

The dough being properly fermented, i.e., when the gluten has matured—this being ascertained by the feel and an examination of the way it stretches—it then passes on to the scaling or dividing process. From the fermentation stage onwards in large bakeries the remaining processes are automatic, and very little variation is possible. The importance of preparing the dough correctly and of fermenting it to the correct stage cannot, therefore, be stressed too strongly.

Dividing the Dough into Loaves.

In small bakeries the dough is "scaled," i.e., weighed by hand; in larger bakeries the dividing of the dough is done by machinery, depending on delivery of a certain *volume* of dough. Dividers are adjustable and can be made to deliver any required volume of dough. A loaf to weigh 2 lbs. is scaled or divided off at 2 lbs. 4 ozs., a 1 lb. loaf at 1 lb. 2 ozs. This additional weight is to allow for the loss of weight in the oven, and evaporation before and after the oven, so that the finished loaf shall weigh not less than 2 lbs. or 1 lb. as required by the law.

The "Hander-up."

After dividing, the dough travels to the next machine, the "hander-up." The "hander-up" is a machine for moulding roughly the dough pieces. At this stage the dough is in a very delicate condition and requires a little rest to recover from the harsh treatment of the divider, which has squeezed and cut it and handled it generally rather roughly. The cut edges want "healing," and it is the purpose of the "hander-up" to close up these cuts and to form a skin all round the piece. In this form, the piece is in the best condition to recover. This period of rest is called "intermediate proof" and lasts for 10-20 minutes.*

"The Moulder."

After recovery, the pieces go through a "moulder," in which it again undergoes a gentle squeezing and pressing action. This renders the condition uniform throughout the piece, so that during the last half hour or so of fermentation (called the "final proof") the expansion and gas formation will be regular. In some bakeries, the same machine serves as both hander-up and moulder. The only essential difference in their action is that the moulder handles the dough much more gently than the hander-up. Both of them tend to set up a state of tension in the gluten network, rendering oven expansion and texture even throughout the loaf.

The Action of the Oven.

The bread has now arrived at the oven and the actual transformation into bread is to take place. The normal temperature for a bread oven is 450° - 500° F. and the time of baking from 40-50 minutes. With brown and other breads the temperature is usually lower and the time longer.

Yeast Activity Increases as the Temperature Rises.

The main changes that take place in the oven are as follows:—For about the first 15 minutes the temperature does not rise above the point at which yeast ceases to be active. If the preceding stages have been carried out accurately, the dough arrives full of life at the oven and as the temperature increases, this yeast activity is also very considerably increased.

The loaf can be seen to rise, owing to the greater development of carbon dioxide and expansion of the gas already contained in it, from a ball which can easily be grasped in one hand until it reaches the well-known dimensions of a 2-lb. loaf.

The temperature of the interior of a loaf never exceeds 100° C., but the exterior can, of course, go much higher. The first stage is the drying out of the outer surface of the dough and the formation of an impermeable skin.

Why Steam is Injected in the Oven.

Up to this point steam can pass out of the interior of the loaf and the loaf can expand. The presence of this steam keeps the skin of the dough flexible. Until steam is produced from the loaf

itself, it is customary to inject steam into the oven. All this while the gluten is coagulating and becoming "set," thus forming a framework for the whole of the loaf.

The Death Point of the Yeast.

About the time the skin is formed, the death point of the yeast is nearly reached and expansion stops. If the fermentation has been carried out, the loaf will keep the shape obtained at this point, the gluten will be strong and able to support it.

Faults Due to Incorrect Fermentation.

If, unfortunately, the loaf has suffered from incorrect fermentation, faults of several kinds will appear, tears in the side of the top crust, later on "flying tops," which is a sufficiently descriptive term not to require further definition. In the interior of the loaf, the bread is gelatinising the starch and making it more easy to digest. It should be mentioned here that there is never sufficient water in a loaf to enable the whole of the starch to be gelatinised, and under the microscope it is possible to detect starch granules in all stages of gelatinisation.

Why Loaves are a Pleasant Brown Colour.

When the crust is dried out, it begins to caramelise. The pleasant brown colour of a loaf is due mainly to caramelisation of the sugar contained in the dough. Now it must be remembered that sugar is one of the important foods that yeast feeds on. There is a certain amount of sugar naturally in the flour, but the bulk of it is obtained by the action of an enzyme called diastase, present in smaller or greater degree in the flour, on starch. The yeast may use up the sugar, however, more quickly than the diastase can produce it, and in some cases there will be a shortage of sugar in the dough when it goes to the oven.

This will be manifested by a paleness in the crumb, the loaf is said to have a poor "bloom," and this detracts from its appearance, a serious point when it comes to selling the loaf.

At the end of three-quarters of an hour, the starch has reached its maximum gelatinisation, the gluten is all coagulated, the outer crust formed firmly all round—the loaf is made.

Bread Must be Cooled Before Wrapping.

In bakeries, where bread is wrapped, care is still necessary. On cooling, the solid crust contracts and small cracks appear through which steam can escape from the interior. If bread is wrapped warm, it will be maintained for several hours in a warm moist atmosphere, which is the ideal condition for the growth of moulds and the development of that bogey of the bread-trade, "rope." It also results in the formation of a soggy crust. It is, therefore, necessary to allow the bread to cool to an extent which will prevent the formation of these conditions.

THE CHEMIST IN THE BAKERY.

It will be seen that once the dough has been made, little can be done by the chemist to alter the course of its fermentation. It has passed into the hands of the technical man. The work of the cereal chemist lies, therefore, mainly in his examination of the raw materials, apart, of course, from such chemico-technical details as temperature control, humidity regulation and other details of factory supervision which are rather outside the scope of this article.

FLOUR.

Flour is examined for the following characteristics:—

(1) Moisture.

Although moisture determination sounds a simple process, it is not so in the case of a substance like flour, which appears to contain water of two types, viz., "free" water which comes off quite readily in a steam oven, and "bound" water, which appears to be in loose combination with the flour. According to the method used and the time the drying is carried out, different figures will be obtained. A vacuum oven method gives figures 1 per cent. higher than a steam oven. As in so many tests on technical materials of an awkward character, it has been found necessary to lay down the conditions of the determination very exactly. The American Association of Official Agricultural Chemists have given a lead in this respect and their official handbook gives a vacuum method of drying in which 2 gm. are heated at 98°-100° C. to constant weight (about 5 hours) in an oven with a vacuum of

25 mm. or less, and a second method in which 2 gm. are heated at 130° C. for 1 hour. This latter is more convenient and is the one usually adopted.

Other Methods.

There are several "quick" methods, one depending on the interaction between the moisture of the flour and calcium carbide, the resulting acetylene producing a pressure which is read off direct in moisture percentages, and another depending on distilling flour with toluene or xylene, when the moisture is carried over into a graduated receiving vessel where it separates and can be read off. Electrical methods depending on the dielectric constant of the condenser in an oscillatory circuit have not proved very satisfactory up to the present.

Moisture in flour in this country may vary from 11 to 16 per cent., and there is no definite general standard. In America, 13.5 per cent. is accepted as fair; Admiralty contracts here call for not more than 12 per cent. and the general run of home milled flour contains 14 per cent. It is this question of moisture that the baker wants to watch carefully, as a difference of 2 per cent. in moisture means about 1s. 6d. per sack to him in dry flour value.



Fig. 4.—TESTING A FLOUR FOR WATER-ABSORPTION.
A weighed amount of flour is put into the small kneader. Water is added from a burette in small increments until the operator considers the dough has attained the correct consistency.

(2) Gluten.

The proteins of flour can be determined by the usual Kjeldahl method, using the factor 5.7 instead of the usual 6.25 to convert the nitrogen figure into the protein figure. This method, however, is lengthy and tedious and does not give as much information as the washing-out method, which, although not scientifically so accurate, is

more useful as a routine test.

The Washing-out Method—

The difficulty about the washing out method to be described is that it depends so much on the personal equation. A standard method has been laid down by the A.O.A.C., but it is not generally adhered to in all laboratories, with the result that if the same sample of flour is sent to a dozen skilled operators, differing figures

will be obtained, which may vary in extreme cases by 1-2 per cent. and more. The wash-water used has an effect, and even in the same laboratory, with two workers of equal experience, difference in the figures may be appreciable. It is essential, therefore, that the same operator should always carry out this test and adopt the same procedure.



Fig. 5.—THE REVOLUTION COUNTER AND GEARS ON THE MIXER.

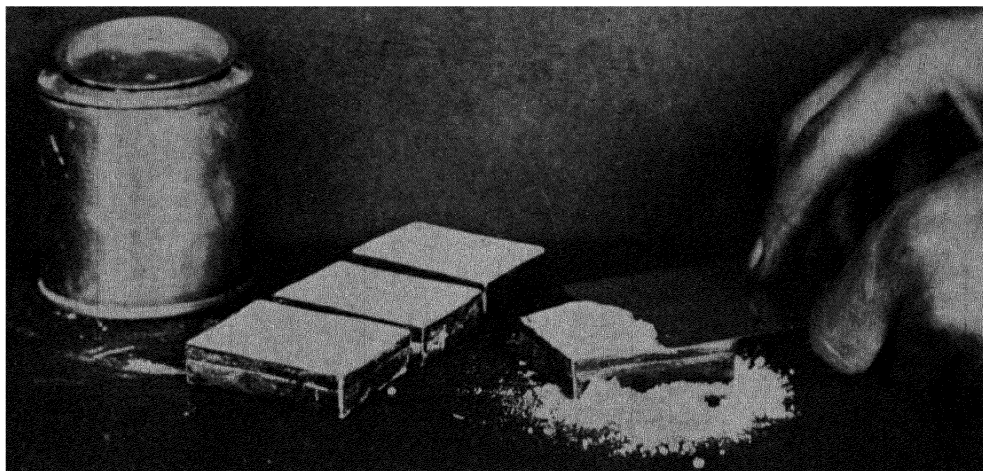


Fig. 6—THE PEKAR COLOUR TEST FOR FLOUR

The flour is pressed flat in shallow copper dishes and wetted, when differences in colour are easily seen

—And How it is Carried Out.

A small quantity of flour (25 or 50 gms.) is weighed out into a small kneading machine and made into a stiffish dough with the requisite amount of water. A revolution counter should be fitted to the kneader, so that the same amount of mixing can be given in all cases. The dough, if fairly stiff, will come away cleanly and wholly from the machine, it is then rolled up into a ball, placed into a beaker of water at 70° F. and allowed to stand for an hour. This period allows the gluten to form more definitely from its constituent proteins. The ball is then submerged in successive lots of water at 70° F., being squeezed so as to expel the starch. The wash-water becomes clearer and clearer and the last lot should be free from starch granules. Some operators work in running water, but the successive method is considered the better. After washing, the gluten is worked into a coherent mass and left in water for half an hour before examining

How the Result is Expressed.

This examination of gluten is a process incapable of expression on paper. It is purely a question of acquired experience. The operator describes the gluten by such terms as "short," "elastic," "tough," "sticky" and so on, and by a consideration of its one or more characteristics

is able to form an opinion as to the quality and origin of the flour from which it is derived

Strength and Absorbing Power.

After the examination for quality, the gluten is spread on a tared filter paper, weighed, dried in an oven to constant weight and weighed again. The ratio of wet to dry gluten is calculated from these figures and gives an indication of its strength and absorbing power. A good home-milled flour should contain about 30 per cent. of wet gluten or more. An average ratio for wet to dry gluten is 3:1. If it is above this, the gluten is always sticky, soft and non-elastic, and should only be used for short fermentation processes. If the ratio is lower than 3, the flour will be "strong," and if much lower than 3, strong and of a low grade.

(3) Water Absorption.

This is again work for an experienced operator. 50 gms. of flour are weighed into the kneader, 0.8 gms. salt and an average quantity, say, 30 c.c. of water added from a burette. This corresponds to 15 gallons to the 280 lb. sack of flour. The mixture is then worked into a dough and the operator feels whether the consistency is too tight or not. If necessary, a little more water is added and worked into the dough until the correct consistency is obtained.

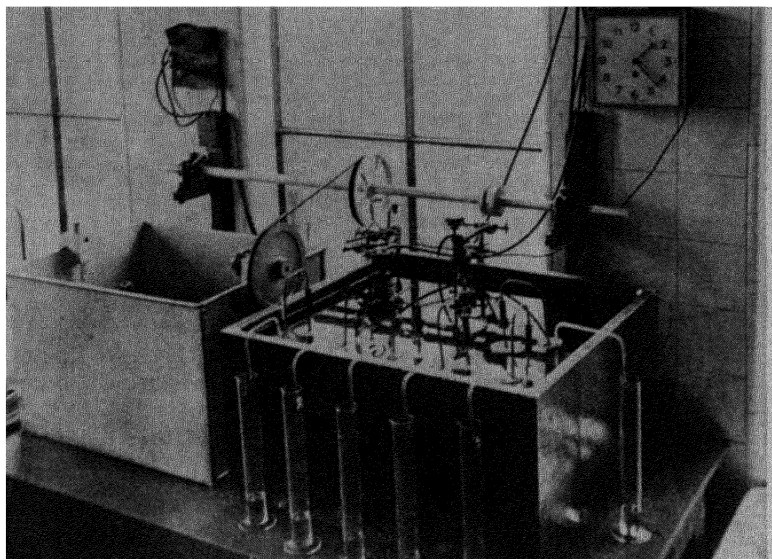


Fig. 7.—APPARATUS FOR MEASURING GAS PRODUCTION.

Used for comparing activities of different yeasts and effects of formula variations, etc.

(4) Colour.

(a) *Pekar Test*.—This is one of the oldest comparative tests for flour quality, and dates back from the days when bleaching was unknown and when the colour of the flour was an almost certain guide to its quality. Flour is placed in a small tray and pressed down and smoothed with a broad spatula so as to make a firm block. A series of these trays is then passed quickly through a basin of water, remaining in only enough to wet the top surface.

Owing to the action of oxydases in the flour in the presence of moisture, the chromogens form coloured products, so that the differences in tint are accentuated. Moreover, specks are more easily seen in the wet surface than the dry. The more numerous these are, the lower the grade of flour.

In assessing the value of flours in this way, it must be borne in mind that the fineness should be approximately the same in all cases. A coarse flour will appear darker than a fine flour of the same quality. Nowadays, the Pekar test has to be interpreted in the light of the result of the examination for bleaching.

—(b) Bleaching.

It has now become standard practice in flour mills to treat their flours with a bleaching process and/or a flour improver. Bleaching arose out of a desire to eliminate or reduce the rather unpleasant shade of yellow in many flours, thus rendering the loaf made from such flours of a whiter and more pleasant colour. It is not adopted in order to try to raise flour of the lowest grades into the highest ;

as a matter of fact, below a certain grade bleaching shows up the bran particles most adversely.

The Bleaching Agents Generally Used.

The most common bleaching agents are nitrogen peroxide which is produced in various ways, and benzoyl peroxide. The former is commonly called the "electric arc" process. The presence of nitrites in flour can be detected by means of the Griess-Ilosvay reagent (a

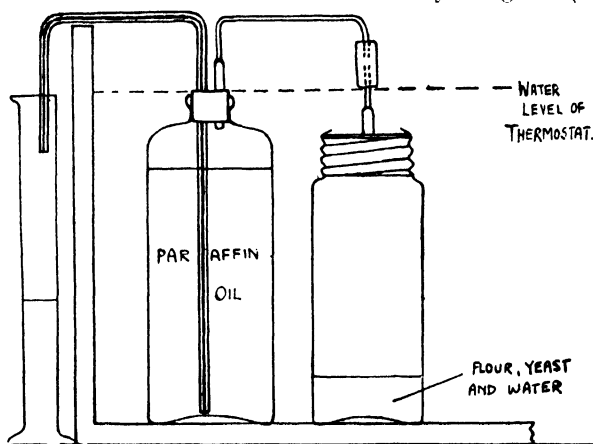


Fig. 8.—DIAGRAM OF APPARATUS USED IN MEASURING VOLUME OF GAS PRODUCED FROM A DOUGH OR BATTER.

The volume of paraffin displaced is measured at frequent intervals.

solution of sulphamic acid in acetic acid, mixed with α -naphthylamine under standard conditions). This reagent is very sensitive and care must be taken at first in interpreting the result, as there are nitrites in the air and they are present to a greater extent in the atmosphere of a laboratory where bunsen burners are alight. A control should always, therefore, be done on a flour known to be unbleached and only if the reaction is definitely positive, can it be concluded that nitrogen peroxide has been used.

Benzoyl peroxide is used at the rate of about $\frac{1}{2}$ oz. to the sack of 280 lbs., and is left as benzoic acid in the flour. The amount present is obviously very small and special standard tests have been devised for its detection.

Some other bleachers such as chlorine are also improvers and are best considered under this head.

(5) Improvers.

Bleachers such as nitrogen and benzoyl peroxides do not in any way interfere with the baking process, but chlorine and other preparations depending on the liberation of chlorine for their action (such as Beta gas, a mixture of chlorine and nitrosyl chloride) and Agene (nitrogen tri-chloride) affect favourably the baking qualities of flour. The underlying idea of these processes is to imitate in home-milled flours the ageing process which takes place in flours kept in store for several months.

Australian milled flours, for instance, arrive in this country and are used in bakeries some three months or more after being milled, and the baker cannot use freshly milled flour with the same advantage as "aged" ones, nor has he the space or the capital to enable him to store flour for three months. Without improvers it would be impossible for the home miller to compete with foreign millers.

Improvers are of two kinds—gases,

mentioned above, and mineral salts, such as acid calcium phosphate and ammonium persulphate.

Test for Presence of Mineral Improvers.

The presence of mineral improvers can be very simply found by shaking the flour up with a heavy liquid such as chloroform or carbon tetrachloride. The mineral matter sinks to the bottom, the flour floats to the top and almost a complete separation can be made. The usual laboratory tests are applied to identify these salts. It is seldom necessary to do more than a qualitative test for any of these materials.

Test for Presence of Ammonium Persulphate.

The presence of ammonium persulphate in flour can be readily ascertained by pouring on to some of the flour doughed up with water a 1 per cent. solution of benzidine in alcohol, when blue spots will indicate the presence of persulphate.

(6) Ash.

This is an important figure to the chemist, as it gives him an indication of the grade of flour—the greater the ash, the lower the grade—provided always that it has not been treated with a mineral improver, as this would remain in the ash after incineration. The ash figure indicates the amount of the bran in the flour, and as this latter increases, the grade of the

flour decreases. The following table gives approximate ranges of ash for the common divisions of flour used in breadmaking.

Patent flour	..	0.30—0.45 per cent.
Straight run	..	0.45—0.55 per cent.
Low grade	..	0.55—0.75 per cent.

The whole berry contains about 2.0 per cent ash, the bran 5.7 per cent. The actual determination is carried out along normal lines.

(7) Diastatic Activity.

A discussion of the methods of deter-

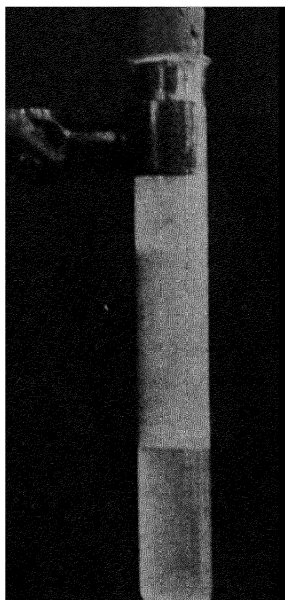


Fig. 9. — SEPARATION OF MINERALS FROM FLOUR.

Phosphates or other added minerals can be detected in flour by sedimentation from a chloroform suspension. The flour rises and most salts are heavy enough to fall to the bottom of the tube.

mining diastatic activity is rather too lengthy a matter for inclusion here and the reader is referred to a standard text book such as Kent-Jones' "Modern-Cereal Chemistry." A certain amount may be learnt from the baking test described later.

The other constituents of flour seldom call for determination, and of the remaining ingredients of the dough batch yeast is the only one that calls for regular attention on the part of the bakery chemist. As regards salt, this is generally of a high standard of purity, and such impurities as are occasionally found in salt seem, if anything, to have a beneficial action on the dough rather than the reverse.

The water used will, normally, be from a known source, carefully watched by a local authority. The nature of the water is, however, important to this extent, that an unduly soft water affects deleteriously the colloidal condition of the dough and will make the doughs "runny." The best water is a medium-hard one and in most cases any defects in the water can be remedied by the use of one of the improvers sold for that purpose.

YEAST.

The only test carried out as part of the bakery routine is one for activity. Moisture is relatively unimportant; yeast contains normally some 75 per cent. of moisture so that 1 or 2 per cent. either way is not of tremendous significance, especially as there is no definite standard for it.

Testing for Activity.

The testing of yeast for activity is carried out in several ways and none of them is over satisfactory. They are, however, on a level with the gluten-washing test—if a worker of experience always carries out the test, he can draw safe

conclusions from the result. Some laboratories test yeast activity by making a dough of standard composition, placing it in standard-sized tins under standard conditions. Others rely on the Hayduck apparatus, which has the advantage that many other materials besides yeast can be tested by means of it. Compared with many other scientific instruments, it is crude and elementary, yet it is doubtful whether there is a more useful single piece of apparatus in the cereal laboratory.

The Apparatus Used.

The apparatus consists of a thermostatically controlled waterbath in which are placed a series of jars each containing a small piece of dough, each prepared under identical conditions in the little kneader already referred to. The yeast is usually made up into a suspension and added from a burette or pipette.

The jars are each connected with a reservoir containing saturated salt solution (in which carbon dioxide does not dissolve to any extent), or paraffin, and as the dough ferments, the gas evolved drives over

the brine into graduated cylinders. The latter are read every half hour or hour according to the conditions used. Great care has to be exercised to ensure there is no leakage.

Some operators use a batter instead of a dough, or even a solution of sugar and yeast nutrients, in which case the gas evolution is greater than with a dough; but there is a great deal to be said for using a dough, because, although the latter is so small as to render it impossible to interpret the results directly into terms of the large masses used in a bakery, yet the yeast is acting under something approaching the conditions it will have in the bakery.



Fig. 10.—THE PERSULPHATE TEST.

The flour is made into a dough. An alcoholic solution of benzidine is added and the presence of persulphates is indicated by bright blue spots.

ROPE.

Only brief reference can be made to this disease of bread. It is a bacterial infection introduced generally in the flour. There are always rope spores in bread and it is only when climatic conditions are favourable (i.e., high temperatures and humidity) that the danger of spoilage from this cause is serious. Fortunately, rope spores only develop slowly in an acid medium, and the addition of acid substances is normally a sufficient preventive.

BAKING TEST.

Many bakeries have no laboratories and in these cases, recourse must be had to a small baking test. It must be emphasised that bulk action plays an important part in fermentation and that the course of fermentation in a small dough, of say, 7 lbs. is quite different from that in a 400 lb. dough, but the experienced baker soon learns what to look for in his small-scale baking test, and is seldom misled.

In cereal laboratories, too, a small scale baking test is advisable, if circumstances permit. This should be done for two reasons —

(1) During actual manipulation of the dough and its progress during the fermentation stage, many facts can be learned which are not brought to light by laboratory tests.

(2) It acts as a confirmation of labora-

tory tests and it is just as well to have this confirmation. Although conclusions drawn from the work in the laboratory are definite and sound in the majority of cases, it occasionally happens that a "queer" flour is encountered, which behaves differently in the bakery from what the laboratory report would indicate.

One can read into this last sentence the fact that laboratory methods for controlling the baker's raw materials are not as complete as they should be. In this respect, however, the baking industry is in company with many other industries and in the hands of a skilled man—and it must

be emphasised that the cereal chemist must be not only skilled but of considerable experience—the results obtained from analytical methods are capable of safe interpretation and he is a man that no large bakery can afford to do without on their staff. Laboratory methods are improving and physical methods are being developed.

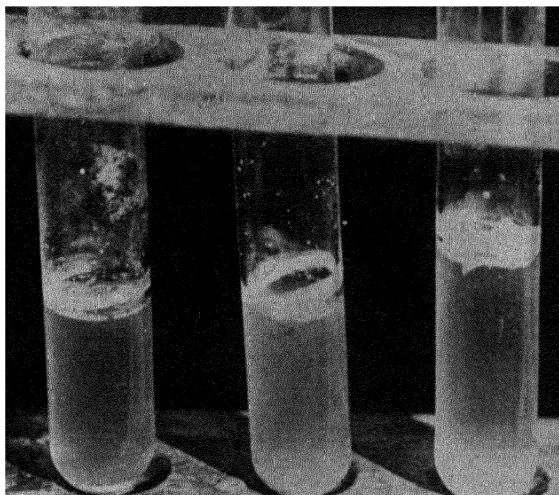


Fig. 11. SKINS OF ROPE (*BACILLUS MENTERICUS*) GROWN IN STERILISED TUBES IN AN INCUBATOR AT 37° C. FROM AN INFECTED FLOUR

The Chopin extensimeter was one of the first "machines" to be introduced for this purpose and the Brabender Farinograph, which depends for its interpretation on a graph representing the power used up by the arms of a kneader in doughing up a mixture of flour and water, is the latest. It is a machine of considerable possibilities and heralds a new line of attack both for routine control and research methods.

CHEMISTRY IN THE GAS INDUSTRY

PART VI.—ANALYSIS OF RAW MATERIALS

By F. E. MILLS, B.Sc., A.M.I.Chem.E.

Proximate Analysis of Coal.

THE methods used in the Gas Industry for the proximate analysis of coal follow closely those described in the British Standard Specification for the Sampling and Analysis of Coal for Inland Purposes.

The methods of sampling are described in detail in the specification and consist generally in collecting a number of increments at regular intervals during the unloading of the consignment. The size and number of the increments depend upon the size of the coal and its ash content, and it is preferable that they should be drawn when the coal is in motion.

Moisture Sample.

The bulk sample is then thoroughly mixed and a "Moisture Sample" of 10 lb. is taken by small increments well distributed over the heap. This sample is quickly sealed and sent to the laboratory, where it is rapidly crushed to less than $\frac{1}{4}$ inch size and reduced to about 2 lbs. by coning and quartering (described below). The sample is spread on a tared metal tray, weighed and then air dried for some hours at room temperature, or at a temperature not exceeding 50°C. , when it is again weighed. It is then ground to pass a 14-mesh sieve and thoroughly mixed. 30 gm. is then taken and

dried to constant weight at a temperature of $105\text{--}110^{\circ}\text{C.}$ in the manner described below.

Preparation of Cone.

The remainder of the bulk sample is crushed to pass through a $\frac{1}{4}$ -in. sieve and is thoroughly mixed by heaping and turning over on to a different place two or three times. The coal is then formed into a cone by depositing each shovelful on the top of the preceding one, care being taken to place it on the apex of the cone. A new cone is then formed twice in a similar manner, the last one being flattened down uniformly and divided into four quarters. Opposite quarters are rejected and the remainder mixed.

This operation is repeated until about 10 lbs. is left. This is crushed and ground to pass a 14-mesh sieve and is then air dried. It is mixed, coned and quartered as before until about $\frac{1}{2}$ lb. is left. This is ground to pass a 36-mesh sieve; it is then mixed and quartered, and the $\frac{1}{4}$ lb. remaining is ground to pass a 72-mesh sieve and finally mixed.

Determination of Moisture.

5 gm. of this air-dried sample is weighed into a shallow weighing vessel provided with a well-fitting cover, such as a glass Petri dish with a ground glass

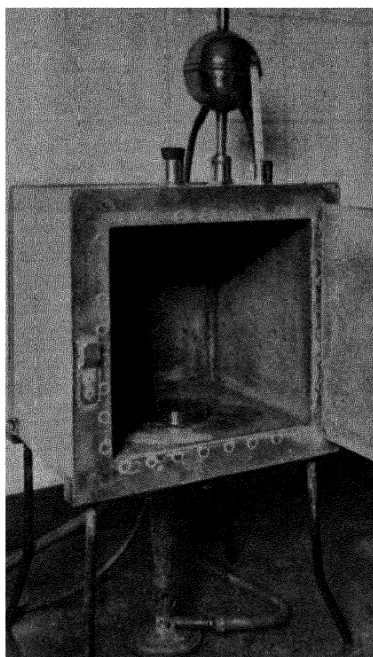


Fig. 1.—DETERMINATION OF MOISTURE IN COAL.

The uncovered coal is heated for one hour in a drying oven.

plate as cover, a shallow silica dish with ground edges and aluminium cover, a shallow stoppered weighing bottle or a pair of watch glasses with ground edges held together with a clip.

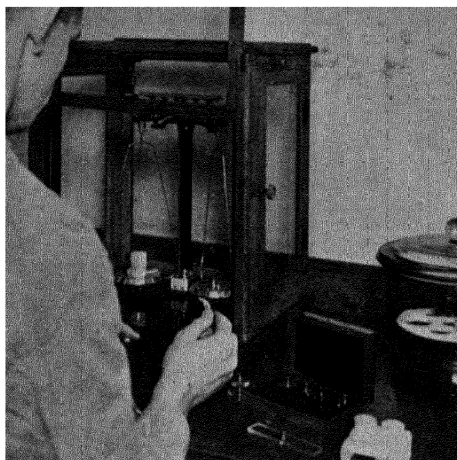
The uncovered coal is heated for one hour in a drying oven capable of being maintained at a temperature of 105-110° C. (See Fig. 1) The cover is then replaced and the covered dish is cooled in a desiccator, and weighed covered.

The loss of weight represents the moisture content of the coal and is expressed as a percentage by weight.

Determination of Volatile Matter.

One gm. of the air-dried sample is weighed into a silica crucible of standard dimensions (see Fig. 2), and is closed by a well-fitting lid. The crucible is then inserted into the hole in a small silica stand.

Heating of the crucible is effected by means of a muffle furnace, one form of which has been specially designed for this work by the staff of the Gas Light and Coke Company and is shown in Fig. 3. This furnace is provided with a thermocouple 1, and by means of a governor de-



IN COAL (1)
The sample of coal is weighed into a silica crucible

vice, the temperature is maintained at $965^{\circ}\text{C} \pm 15^{\circ}\text{C}$. In order to prevent oxidation of the coal during heating, nitrogen (free from oxygen) is passed from tube 2 into the muffle through the tube carrying the thermocouple, at a rate of about $\frac{1}{2}$ cub. ft. per hour, and emerges through a tube in the door, the latter making a tightly fitting joint.

The stream of nitrogen is admitted to the muffle for about two minutes, and the crucible in its stand is inserted into the muffle up to the stop formed by the end of the thermocouple sheath (see Fig. 3) and the door is closed. Heating is continued for seven minutes, after which the crucible is cooled in a desiccator and re-weighed.

The loss of weight is expressed as a percentage of the weight of coal taken and from this is subtracted the percentage of moisture.

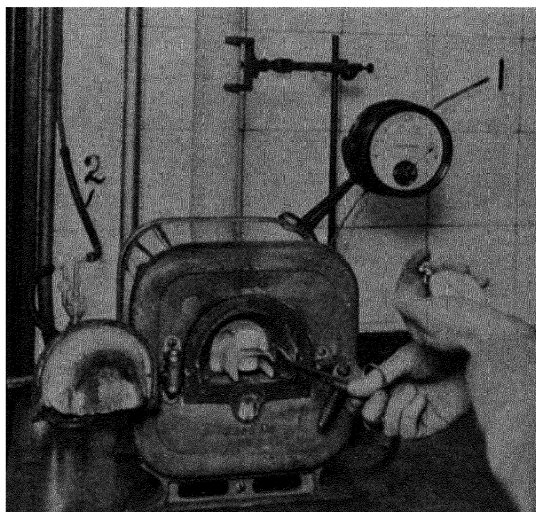


Fig 3—DETERMINATION OF VOLATILE MATTER IN COAL (2)

The crucible, on a silica stand, is placed in a muffle furnace for seven minutes, at a temperature of 965° C. (1) Pyrometer, (2) Tube supplying nitrogen to the muffle to prevent oxidation

Alternative crucible method.

If a muffle furnace, such as that described above, is not available, the determination of volatile matter may be performed by using an ordinary burner, such as a Meker burner, provided with a cylindrical shield of asbestos, suit-

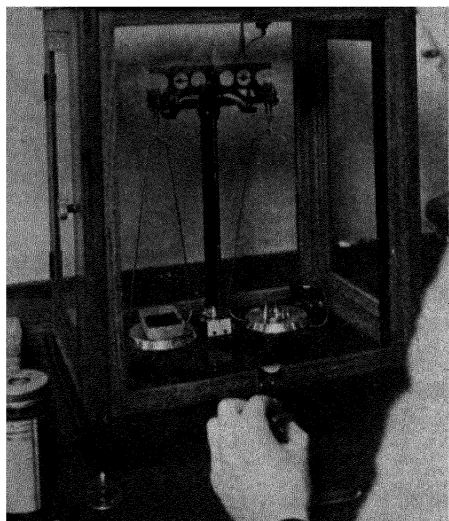


Fig. 4. —DETERMINATION OF ASH IN COAL (1).
The sample is weighed into a shallow silica dish.

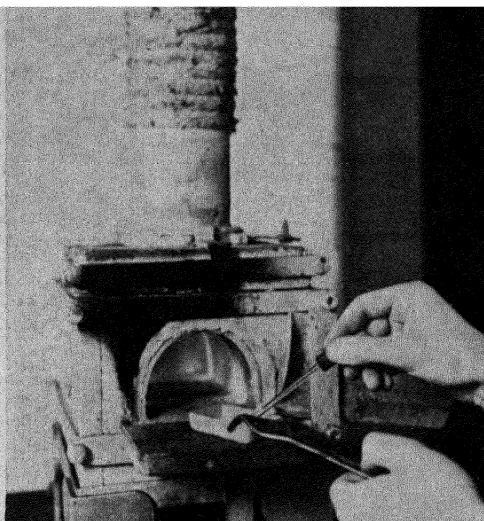


Fig. 5. —DETERMINATION OF ASH IN COAL (2).
The silica dish is inserted into an open-ended muffle furnace at $800^{\circ}\text{C}.$, until combustion is complete.

ably supported, to prevent excessive heat losses due to convection and radiation.

In this case, only a platinum crucible of standard dimensions is used, closed by a well-fitting lid, which may be provided with a hole in the centre of not more than 2 mm. diameter. The crucible is suitably supported by means of a nichrome wire triangle and is so placed that only the outer cone of the properly aerated flame is in contact with it.

The heating is such that a temperature of $965^{\circ}\text{C.} \pm 15^{\circ}\text{C.}$ is maintained in the bottom of the covered crucible, as indicated by the incipient fusion of a crystal of pure potassium chromate placed in the crucible and heated for seven minutes under the conditions of the determination. When this temperature has been correctly attained, the gas pressure is kept constant as indicated on a suitable pressure gauge.

One gm. of the air dried coal is weighed into the crucible, the lid is inserted, and the whole is placed upon its support over the burner for a period of seven minutes. The crucible is then quickly cooled by placing on a cold iron slab to prevent oxidation of the contents, after which it is placed in a desiccator and re-weighed when quite cold.

As before, the loss of weight is expressed as a percentage by weight of the coal

taken, and the percentage of moisture is subtracted from this figure.

Determination of Ash.

5 gm. of the air-dried sample is weighed into a shallow silica dish (see Fig. 4), and the dish is inserted into a muffle furnace maintained at a temperature of about 800°C. The end of the muffle is left open in order to maintain an oxidising atmosphere (see Fig. 5).

In order to prevent mechanical loss, the coal is heated slowly in the mouth of the muffle until the volatile matter has been expelled, after which it is pushed into the hotter part of the muffle.

When combustion appears to be complete, the ash is moistened with a few drops of alcohol. If black specks appear, the alcohol is gently burnt off and the residue is ignited again until combustion is complete.

The dish is then cooled in a desiccator and re-weighed. The weight of the ash is expressed as a percentage of the weight of the coal taken.

Analysis of Gas Oil.

Physical tests on gas oil are used to check uniformity of deliveries and are determined in the manner described in the Standard Methods of the Institution of



Fig 6—ANALYSIS OF GAS OIL (1)

Determination of unsaturated hydrocarbons. The oil is shaken with twice its volume of 80 per cent sulphuric acid in a separating funnel.

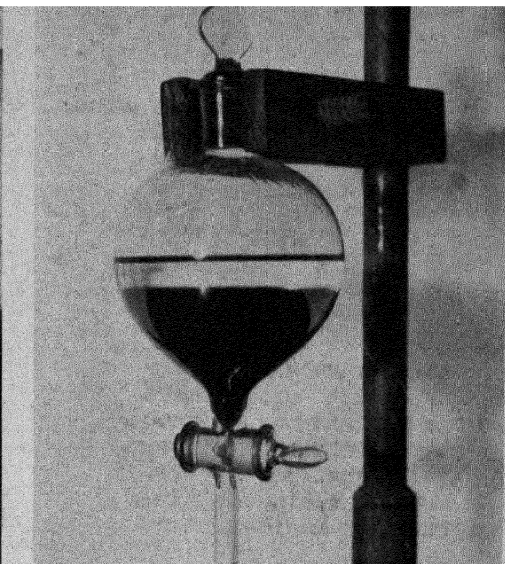


Fig 7—ANALYSIS OF GAS OIL (2)

Determination of unsaturated hydrocarbons. The separating funnel is allowed to stand for two hours, and the lower layer of acid is run off.

Petroleum Technologists. They have been referred to in the sections dealing with the chemistry of petroleum and its products.

For the purpose of assessing the value of gas oil for gas-making purposes, it has been shown by R. H. Griffith* that a chemical analysis is of more value than purely physical tests. He has published a method of determining the content of aromatic, unsaturated, paraffin and naphthene hydrocarbons, and has shown how the results therefrom may be correlated with the thermal yields obtainable in the gas-making process.

The method of analysis is briefly as follows:

The Distillation Curve.

200 ml. of the oil is distilled from a 250-ml. Jena flask of standard size, in the distillation apparatus described in the Methods of the Institution of Petroleum Technologists, at such a rate that the whole process takes 45-60 minutes.

The volumes collected at intervals of 10-15° are noted in order to construct a distillation curve, and the distillation is continued to a suitable end-point, about 340-380° C.

* R. H. Griffith, J.S.C.I., 1928, **47**, 217; 1929, **48**, 250T.

The Unsaturated Hydrocarbons.

50 ml. of the total distillate is then shaken for 15 minutes with 100 ml. of 80 per cent sulphuric acid in a separating funnel (see Fig. 6). After standing for two hours, the acid layer is run off (see Fig. 7), and the residual oil is washed with water. The washed oil, as free as possible from water, is then transferred to a 100-ml. flask and is distilled to the same end-point as that reached in the original distillation. The difference in volume before and after this treatment is due to the removal of unsaturated hydrocarbons.

The Aromatic Hydrocarbons.

20 ml. of the unsaturated free oil is then shaken for 15 minutes with 50 ml. of concentrated sulphuric acid. After standing for two hours, the oil which separates is washed with water as before, and its volume is measured directly, with careful draining of the separator. The difference in volume before and after this treatment is due to the removal of aromatic hydrocarbons.

The residual oil consists of paraffins and naphthenes, and it is dried overnight by calcium chloride before proceeding to the next stage.

THE CHEMISTRY AND PHARMACY OF VEGETABLE DRUGS

PART XI.—ALKALOIDAL DRUGS. 5. Ephedra, etc.

By NOEL L. ALLPORT, A.I.C.

Assistant Analyst, The British Drug Houses, Ltd.

EPHEDRA, or Ma Huang, is said to have been employed medicinally by the Chinese 5,000 years ago, but it has only become prominent in Western medical practice during the last 10 years. Owing to its value in the treatment of asthma, it is now a drug of considerable importance.

Description of the Drug.

The ephedra of commerce consists of the dried young branches of various species, including *Ephedra sinica* and *E. equisetina*, natives of China; and of *E. Gerardiana* and *E. nebrodensis*, both indigenous to India. The drug consists of switches of thin, sub-cylindrical, green stalks, arising from stouter brown woody branches which in their turn are attached to still thicker stems. The green stalks vary from 7 to 30 cm. in length and may be about 2 mm. in diameter at their thickest part; they are characterised by bearing diminutive leaves in opposite pairs at intervals of about 4 cm. (Fig. 2.)

Botanical Classification of Ephedra.

Ephedra occupies a position of peculiar interest in the

general classification of the vegetable kingdom, since it belongs to one of the three genera which constitute the class of Gymnosperms called Gnetales. The Gymnosperms, in which the seeds are situated on an open scale instead of being provided with a seed vessel as in the true flowering plants, or Angiosperms, are the

smallest division of the vegetable kingdom, embracing only 14 per cent. of the known species, as compared with 59 per cent. belonging to the Angiosperms. Although the Gymnosperms include the Conifers and may seem abundant in

some areas, yet when the whole world is considered the Angiosperms are unquestionably the dominant division, growing in the utmost profusion and capable of adapting themselves to mountainous regions of perpetual snow or to the almost rainless wilderness of African deserts. In untold ages past, from the end of the Carboniferous to the beginning of the Cretaceous era, the Gymnosperms were the pre-eminent flora and the most highly

organised plants of the world.

It is therefore interesting to observe that ephedra belongs to a very

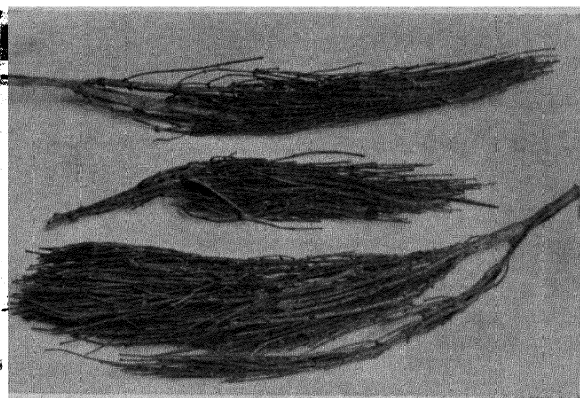


Fig. 1.—CHINESE EPHEDRA.

This drug is imported in bales weighing from 2½ to 4 cwt.



Fig. 2.—EPHEDRA.

In this drawing the pairs of opposite rudimentary leaves at each node are clearly represented.

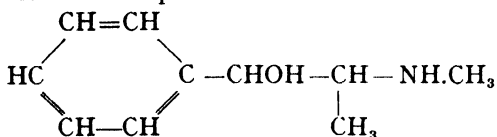
CLASSIFICATION OF THE GYMNASPERMS : SHOWING THE POSITION OF EPHEDRA.

CLASS.	LIVING OR EXTINGUISHED	PRINCIPAL REPRESENTATIVE.	REMARKS.
Pteridospermæ	Extinct ..	Lyginodendron	Possessed characters intermediate between the Ferns and Cycads. Extinct before the commencement of the Mesozoic era.
Cycadales ..	About 100 species still living.	Cycas	Superficial resemblance to palms; live 1,000 years or more Possess the largest motile spermatozooids known in any living organism.
Bennettitales ..	Extinct ..	Dacotensis and Gibsonianus (Luccombe Chine fossil)	Possessed many points of resemblance to the Angiosperms
Ginkgoales ..	One species still living	Maidenhair tree	Cultivated in gardens in the East Dioecious and has motile spermatozooids
Cordaitales ..	Extinct ..	Cordaites ..	Possibly forerunners of the Conifers
Coniferales ..	Living ..	Pines, cypresses, yews	Largest class of Gymnosperms Spermatozooids non-motile
Gnetales ..	About 40 species living: 35 belonging to Ephedra	Ephedra ..	Anatomy of this class shows close resemblances to the structure of Angiosperms

small class of Gymnosperms, revealing in their structure marked resemblances to the Angiosperms and thus possibly being near relatives of those transitional types that must have existed during the Cretaceous period to herald the advent of the true flower. Since then the whole of the Tertiary cycle of the world's history has come and gone, and during the passage of that unimaginable time the pride of the Gymnosperms has faded and the flowering plants have become undisputed lords of the vegetable kingdom.

Chemistry of Ephedra.

The physiologically active principles are the alkaloids ephedrine and its stereoisomeride pseudo-ephedrine. The graphical formula for ephedrine is:—



and it is seen that, for an alkaloid, its structure is relatively simple. When isolated and purified it occurs as a deliquescent white crystalline solid freely

soluble in water and melting between 38° and 42° C. Small quantities of the N-methyl derivative of both ephedrine and pseudo-ephedrine are also present in the drug. The total alkaloidal content varies between about 1 and 2 per cent., of which 60 to 70 per cent. is ephedrine.

Test for Ephedrine.

Unlike the majority of alkaloids, ephedrine does not yield any precipitate when its acid solutions are treated with Mayer's reagent. If a solution of a few milligrams of the alkaloid, or of one of its salts, in 1 ml. of water is treated with a drop of copper sulphate solution followed by about 1 ml. of sodium hydroxide solution, a violet colour is produced. When this liquid is shaken with a little ether and the immiscible liquids allowed to separate, the ethereal layer is coloured purple and the underlying aqueous portion becomes blue.

If ephedrine is dissolved in chloroform and the solution allowed to stand for some hours, the base is converted into the hydrochloride and crystals of this salt separate as a crystalline precipitate. This test distinguishes ephedrine from pseudo-ephedrine.

Assay of Ephedra.

The process for the evaluation of this drug follows on the general lines for the determination of alkaloidal content, but certain special details of technique must be observed. Since the alkaloids are freely soluble in water it is necessary to saturate the alkaline aqueous extracts with sodium chloride before shaking out with ether. Again, the ephedrine base is very readily volatilised when warmed and it is therefore necessary to avoid evaporating its ethereal solutions to dryness on the water-bath. The separation of ephedrine from pseudo-ephedrine may be accomplished by treating the mixed hydrochlorides with chloroform, in which ephedrine hydrochloride is insoluble.

Determination of Total Alkaloids.

The drug is powdered and 20 gm. is macerated for a few minutes with 200 ml. of a mixture of 3 volumes of ether and 1 volume of chloroform. About 10 ml. of 10 per cent. ammonia solution and 1 gm. of anhydrous sodium carbonate are added and, after shaking frequently during four hours, the mixture is allowed to stand overnight. It is then transferred to a percolator and extracted, first with 100 ml. of the ether-chloroform mixture, then with ether itself until all alkaloid has been removed. The colour test already described may be applied to a few drops of the percolate to ascertain when the drug is exhausted. The percolate is transferred to a separating funnel and shaken with four successive portions of dilute hydrochloric acid; the acid shakings are mixed together, filtered, and the filter washed with a little more dilute acid. The filtrate is nearly neutralised with sodium hydroxide solution, transferred to a separating funnel, 10 gm. of anhydrous sodium carbonate and sufficient sodium chloride to saturate the liquid are added, and the mixture is shaken until the solids are dissolved. The aqueous solution is extracted with five separate portions of ether, the separated and combined ether extracts allowed to stand until clear, and then decanted through a pleated filter into a beaker. The ethereal solution of the alkaloids is warmed and poured off from crystals of sodium chloride, which usually separate at this stage, into a flask. The bulk of the ether is distilled off and the remainder allowed to evaporate spon-

taneously without the application of heat. The alkaloidal residue is dissolved in excess of decinormal sulphuric acid, the solution diluted with a little water and titrated with decinormal sodium hydroxide using methyl red as indicator. Each millilitre of decinormal acid is equivalent to 0.01651 gm. of total alkaloids calculated as ephedrine.

Determination of Ephedrine Hydrochloride.

The alkaloidal liquid, after being titrated, is transferred to a separating funnel, rendered alkaline with sodium carbonate and saturated with sodium chloride. The alkaloids are extracted with several portions of ether, and the latter evaporated to low bulk. The alkaloids in the ethereal solution are then precipitated as hydrochlorides by rendering just acid to litmus paper with an alcoholic solution of hydrogen chloride gas. This acid liquid should be introduced from a capillary tube, the ether being well agitated in the meantime, thus avoiding the addition of more than the slightest excess of acid. The precipitated alkaloidal hydrochlorides are filtered off on a sintered glass crucible, washed with a saturated ethereal solution of ephedrine hydrochloride, and dried at 80° C. The ephedrine hydrochloride is separated from the pseudo-ephedrine hydrochloride by macerating the dried mixture with dry chloroform, which dissolves the latter salt, and collecting the insoluble ephedrine hydrochloride in a tared Gooch crucible, drying at 80° C., and weighing.

Pharmacy of Ephedra.

The isolated alkaloidal salts are almost exclusively used in medicine in preference to preparations made directly from the whole drug. Ephedrine hydrochloride, which is official in the British Pharmacopœia 1932, occurs as odourless, colourless crystals, soluble in water forming a neutral solution.

Isolation of Ephedrine as Hydrochloride.

The extraction of the alkaloids on a large scale may be conducted by macerating the powdered drug with 0.5 per cent. aqueous solution of hydrochloric acid for several hours and then pressing out the liquor and extracting the marc a second time with more acid. The mixed extracts are filtered, neutralised with sodium

carbonate, evaporated to low bulk, and then rendered strongly alkaline with sodium carbonate and the mixture again filtered. The filtrate is saturated with sodium chloride, the alkaloids extracted with ether, and most of the solvent removed by distillation. The concentrated ethereal solution is carefully acidified with an alcoholic solution of hydrogen chloride, the precipitated alkaloidal hydrochlorides filtered off, and dried. The pseudo-ephedrine hydrochloride is removed by treatment with dry chloroform, leaving the ephedrine hydrochloride, which may be further purified by recrystallisation from alcohol.

Pharmacology of Ephedrine.

The physiological action of ephedrine resembles that of adrenaline, with the additional advantages that, unlike the latter, it can be administered orally and its effects are more prolonged. About 1 gr. of ephedrine hydrochloride, given by

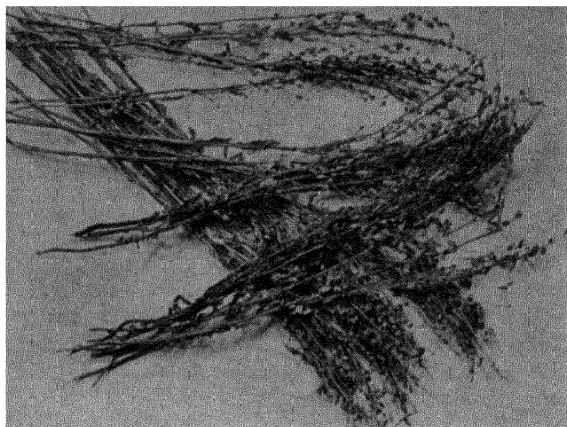


Fig 3 LOBELIA
The numerous capsular fruits are easily seen, but the leaves are shrivelled. It is imported in bales weighing from 1½ to 2½ cwt.

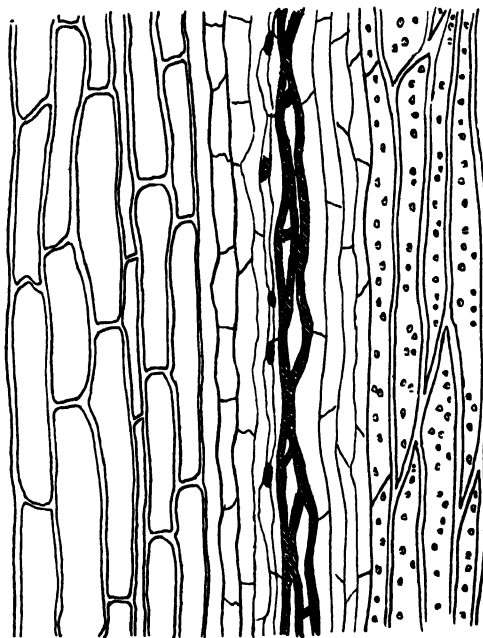


Fig 1 - MAGNIFIED DIAGRAMMATIC DRAWING OF A RADIAL SECTION OF LOBELIA STEM

The dark tube-like structures are the laticiferous vessels which anastomose with one another, forming characteristic tissue elements which can be readily isolated from the rest of the plant by digesting with potassium hydroxide solution. Immediately to the right of the laticiferous vessels are the bast and cambium, and to the left the endodermis. The large cells on the extreme left compose the cortex, while the pitted cells on the right constitute the woody tissue.

the mouth, produces an increase in blood-pressure with decreased rate of heart-beat lasting for approximately two hours. Like adrenaline it will dilate the pupils and has been successfully employed in ophthalmological work. A 1 per cent. solution of ephedrine alkaloid in light paraffin forms a useful

spray for the alleviation of hay fever.

As an alternative to injections of adrenaline, ephedrine is most valuable for relieving the spasms of asthma. The spasmotic attacks suffered by asthmatic persons are due to the muscles of the bronchioles contracting and thus reducing the cross-sectional area of the membranes which divide the blood capillaries from the chambers of air intake. This condition causes acute distress, since it is across these membranes that the exchange by diffusion of oxygen and carbon dioxide takes place between the inbreathed air and the blood. The administration of ephedrine

effectively relaxes the muscles of the bronchioles and thus affords rapid relief.

LOBELIA.

This drug consists of the whole, dried, flowering plant of *Lobelia inflata*, or Indian tobacco, an annual herb indigenous to the eastern United States. The angular yellow or purplish stems

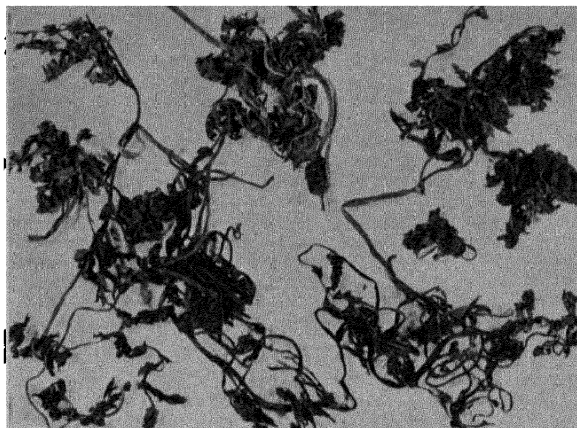


Fig. 5.—CONIUM HERB.

This shows the dried material. Many of the galenicals were made from the fresh herb. Owing to its uncertain action the drug is now rarely prescribed.

average about 30 cm. in length. As seen in commerce the leaves are much broken and inconspicuous, but the two-celled capsular fruits are abundant. The drug possesses a slightly irritating odour and a burning acrid taste. When the stem of the growing plant is wounded a milky juice exudes which is contained in the laticiferous vessels which ramify throughout both stem and leaves (Fig. 4).

Chemistry of Lobelia.

The principal physiologically active constituent of the drug is the dextro-rotatory alkaloid lobeline, $C_{22}H_{29}O_2N$, which crystallises in broad colourless needles melting at 130° to 131° C. A second alkaloid termed lobelidine, $C_{20}H_{25}O_2N$, has also been isolated. The separation of these two alkaloids has been effected by repeatedly extracting an aqueous solution of the mixed hydrochlorides with chloroform, which removes the lobeline but not the lobelidine. Lobeline forms well-defined crystallised salts. The total alkaloidal content of the drug is stated to vary between 0.5 and 0.7 per cent.

Assay of Lobelia.

The assay of this drug may well be a matter of importance in the near future, since the Poisons Board, constituted under the Poisons and Pharmacy Act, 1933, has proposed in their Draft List of Poisons, issued in August, 1934, that preparations

containing over 0.1 per cent. of the alkaloids of Lobelia should be scheduled as poisonous substances in Part I of the list.

The alkaloidal content of the crude drug may be determined in the following manner:—

Fifteen gm. of the finely powdered material is macerated with 150 ml. of a mixture of ether 5 vols.

and chloroform 1 vol. After 10 minutes, 5 ml. of dilute ammonia is added, the mixture is shaken at intervals during 2 hours, and 15 ml. of water is added to agglomerate the drug. The supernatant solvent is filtered through a plug of cotton wool, and 100 ml. (equivalent to 10 gm. of the drug) is transferred to a separating funnel and the alkaloid extracted with dilute sulphuric acid. The mixed extracts are rendered alkaline with ammonia and the alkaloids again extracted with ether, each portion of the latter being washed in succession with the same portion of water contained in another separating funnel and then transferred to a flask. The ethereal solution is distilled to low bulk, the remainder of the solvent allowed to evaporate spontaneously, the alkaloidal residue dried *in vacuo* and either weighed, or determined by adding an excess of decinormal acid and titrating back with decinormal sodium hydroxide, using methyl red as indicator. In the latter case 1 ml. of decinormal acid is equivalent to 0.028519 gm. of total alkaloids calculated as lobeline.

Assay of Galenical Preparations.

The evaluation follows on similar lines to the method described for the crude drug. A measured quantity is introduced into a separating funnel, acidified with dilute sulphuric acid, and vegetable extractive material removed by shaking with ether, the latter being rejected after

washing with a portion of dilute acid contained in another separating funnel. After adding the acid washing to the main bulk of the aqueous liquor in the first separating funnel, and rendering the mixture alkaline with ammonia, the alkaloid is extracted with ether and the assay completed as already indicated for the powdered drug. For the assay of weak tinctures, 100 ml. or more should be evaporated to low bulk before commencing the extraction.

Pharmacy of Lobelia.

Preparations of lobelia are employed in the treatment of asthma although its use is now declining. Lobeline itself has a physiological action resembling that of nicotine; it first excites nerve cells and then paralyses them.

Compound lobelia powder contains 25 per cent. each of lobelia, stramonium, tea leaves, and potassium nitrate together with a trace of oil of anise. The fumes produced by its burning are inhaled for the relief of asthma.

Ethereal tincture of lobelia is a 1 in 5 preparation made by percolating the powdered drug with spirit of ether (ether 1 vol., alcohol 2 vols.). This is employed as an anti-spasmodic and expectorant for the treatment of bronchitic asthma. The simple tincture of lobelia is made with 60 per cent. alcohol by the standard percolation process (see Vol. 1, page 43) and is also used for asthmatic complaints.

CONIUM OR HEMLOCK.

The spotted hemlock, *Conium maculatum*, grows wild in Great Britain and throughout temperate Europe and Asia. It is to be found as a handsome herb, 1 to 2 metres high, growing on hedge banks



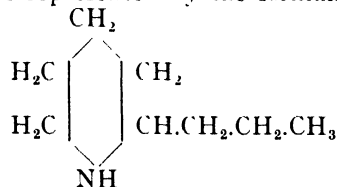
Fig. 6—CONIUM OR HEMLOCK

This shows the form of the plant when growing. Note the characteristic spots on the stem. The drawing of the fruit is on a much larger scale than that of the whole plant. The fruits are only about 3 mm. long, but the plant may reach a height of 2 metres.

and near the borders of fields. The hollow, smooth, greenish stems are marked with dark purple spots, and when the plant is crushed it emits a disagreeable odour similar to that associated with mice. The dried material of commerce consists of ill-defined greyish-green pieces of plant material which do not admit of precise description. The ripe fruits are yellow but for medicinal purposes they should be gathered while still green; they occur as longitudinally fissured ovoid bodies about 3 mm. long and in commercial specimens the mericarps (half fruits) are usually separated.

Chemistry of Conium.

The drug contains the alkaloids coniine, γ -coniceine, conhydrine, methyl-coniine, and pseudo-conhydrine. Coniine was the first alkaloidal substance to be synthesised (see Vol. 1, page 38). Its constitution may be represented by the formula:—



The herb, apart from the fruits, contains approximately 0.2 per cent. of total alkaloids, while the fruit often yields upwards of 2 per cent.

Assay of Conium.

Coniine is a liquid alkaloid which readily volatilises when warmed, and in order to determine the alkaloidal content of the drug it is best to convert the extracted bases to the hydrochlorides and to weigh

the salts. Pure coniine hydrochloride occurs as colourless crystals melting at about 212° C. The following process of assay is convenient :—

Five gm. of the dried and powdered fruit (or 25 gm. of the whole herb) is extracted for 2 hours in a Soxhlet apparatus (see Vol. 2, page 505) with a solvent consisting of chloroform 5 vols., absolute alcohol 3 vols., and a saturated solution of hydrogen chloride gas in chloroform 2 vols. The cooled extract is transferred to a separating funnel, shaken with three portions of water, and the separated aqueous layers washed in turn with successive portions of chloroform. The chloroform washings are rejected, the aqueous layers bulked, made alkaline with sodium hydroxide, and extracted with several portions of chloroform. The chloroformic solution of the alkaloidal bases is transferred to a tared flask, rendered just acid by the addition, from a capillary tube, of an ethereal solution of hydrogen chloride gas, the solvent then distilled, and the residue of alkaloidal hydrochlorides dried at 80° C. and weighed.

Pharmacy of Conium.

Conium possesses a depressant action on the motor nerves and was at one time employed in the treatment of chorea and mania, while as an antispasmodic it has been tried in cases of whooping-cough and

asthma. The drug is mentioned in Anglo-Saxon medical literature and during the nineteenth century was much employed by physicians, but owing to its uncertain action it is now rarely administered internally. Coniine hydrobromide dissolved in a gelato-glycerin base is occasionally used as an external application for hæmorrhoids. The British Pharmacopœia of 1885 included both the whole herb and the fruit besides many galenicals prepared from them. The number of preparations was curtailed in the next edition (1898), and the drug finally omitted altogether in the Pharmacopœia of 1914.

Toxicology of Conium.

As a poison the drug is specially interesting owing to the expressed juice of the fresh plant having been chosen by the ancient Greeks as the instrument of capital punishment. The practice has been described as a humane custom, on the supposition that death following the draught of hemlock juice is painless, and judging from the available toxicological evidence there would seem to be some justification for this statement. The symptoms of a fatal dose generally commence with dizziness and weakness of the legs, which after some hours deepens into paralysis of all the limbs accompanied by stupor and slight convulsions. The light fades, the enfeebled respiration fails and the life of the victim glides to infinitude.

FIRE EXTINGUISHERS

THE importance of this group of substances applies not only to normal outbreaks of fire, but more especially to those that occur in chemical, paint and petroleum factories, etc. It is not usually recognised that substances such as acetic acid will burn.

Fire extinguishers of the chemical variety belong to three types: solid, liquid and gaseous.

The solid form includes those which evolve carbon dioxide on heating and obviously includes bicarbonates or carbonates and some clay or other material to prevent caking.

The liquid variety is of several types. There are firstly those that are composed of non-inflammable organic liquids such

as carbon tetra-chloride, ethylene dichloride and, more recently, fluoro-paraffins. Of the second type are the two-solution fire extinguishers. Some are merely composed of a receptacle containing separated acid and bicarbonate solutions which on application are made to mix and so produce carbon dioxide. The well-known "Foamite" type consists of two solutions, one of aluminium sulphate and the other of sodium bicarbonate. Liquorice or a similar foam-producing medium is added to enable the mixed solutions to cling to the burning surface.

Gaseous carbon dioxide is also now employed. Actually this substance is stored in cylinders in the liquid form, which on release of pressure changes to a gas.

ADIABATIC FUEL CALORIMETRY

PRACTICAL METHODS OF USING THE PARR BOMB CALORIMETER

By A. E. BEET,

Department of Fuel Technology, Sheffield University

WHEN using the usual forms of calorimeter provided with heat-insulating jackets or walls there is always a transference of heat from or to the calorimeter during a determination. This necessitates the application of radiation corrections if accurate results are to be obtained, and though the method of calculation of such corrections has been carefully worked out, there yet remains a tedious series of thermometric readings before the amount of correction to be applied can be calculated. (See pp. 139, *et seq.*)

It will readily be seen that if such heat loss or gain could be prevented the determination of calorific value would be much simplified. This may be achieved by surrounding the calorimetric system with a water-jacket containing a large volume of water, the temperature of which can be varied so that it is always at the same temperature as the calorimeter throughout the determination. The rise in temperature then observed in the calorimeter is the true rise, and the product—Rise $\times$ Water Equiva-

lent of Calorimeter gives the number of heat units liberated during the combustion.

If a large number of determinations are made, it is a good idea to construct a ready-reckoner, so that calorific powers (both in calories/gramme and B Th.U/lb.) can be read off directly when the rise in temperature has been obtained. This "adiabatic" method of calorimetry was devised by the late Professor T. W. Richards, and its application to practical fuel calorimetry was the work of the late Professor S. W. Parr.

THE APPARATUS.

The general arrangement of the Parr adiabatic calorimeter is seen in Figs. 1 and 1A. There are three main parts:

(a) the bomb, (b) the bucket, and (c) the water-jacket, which carries the stand for the two thermometers and also pulleys for working the stirrers.

The Bomb.

(See Fig. 2.)

This is cylindrical and made of a non-corrodible nickel-chromium alloy (Inconel) invented by the late Professor S. W. Parr, who designed the

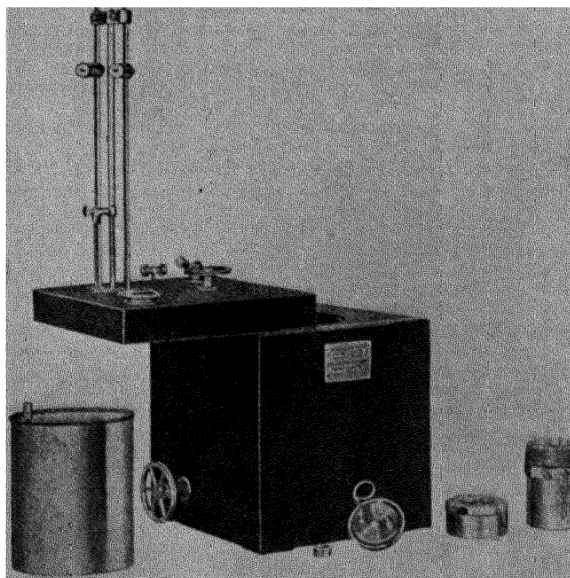


Fig. 1—THE ADIABATIC CALORIMETER

whole apparatus. Three illium studs on the bottom of the bomb allow of an efficient circulation of water underneath the bomb. Its lid, also of illium, is held in place by an octagonal nickel plated steel screw cap, and a gas-tight joint is made by a hard rubber washer fitting in a circular groove in the lid. Two illium rods are fastened to the lid; the upper end of one of them is electrically insulated from the bomb by a conical vulcanite sleeve, there being a terminal outside the bomb. The other rod is looped at its lower end to support the small illium capsule holding the charge of combustible substance. The lid is also fitted with a non-return valve seated on a small rubber washer and pulled home by a spiral spring. This type of valve simplifies the filling of the bomb with oxygen, preparatory to a determination.

The Bucket or Calorimeter Vessel.

(See Fig. 1.)

This is made of nickel-plated copper, is oval in cross section, and fitted with a wire handle which folds out of the way during the

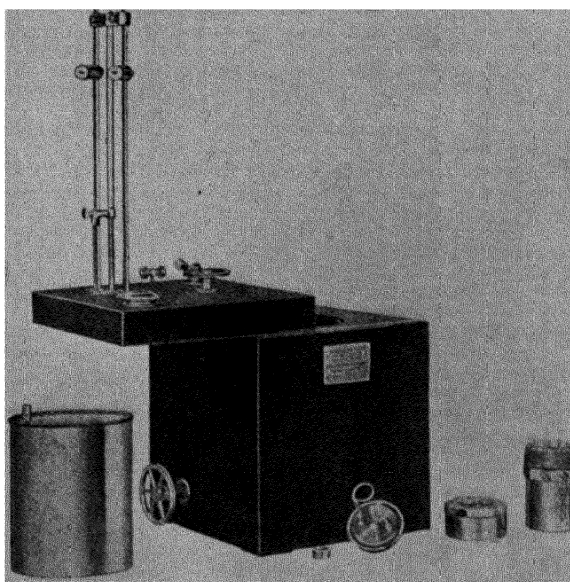


Fig. 1A.—THE ADIABATIC CALORIMETER. Showing the hot and cold water supply, measuring flask and motor for driving pump and stirrers.

determination. Mounted on brackets at one end of the oval is a stirrer with three screw paddles which rotate at 150 r.p.m. An indented circular portion on the base of the bucket correctly positions the bomb during a determination.

The Water-Jacket.

(See Figs. 1 and 3.)

The water-jacket is cubical, of tinned copper, and covered on the outside with bakelite. It is fitted with a hollow lid of the same materials which can be swung to one side only when the cam lever is raised and when the two thermometers have been moved out of danger from shearing. An oval space slightly larger than the bucket is provided in the inner wall of the jacket, the bucket resting on a vulcanite stand. On the bottom of the oval space is a spring contact stud for completing the firing circuit.

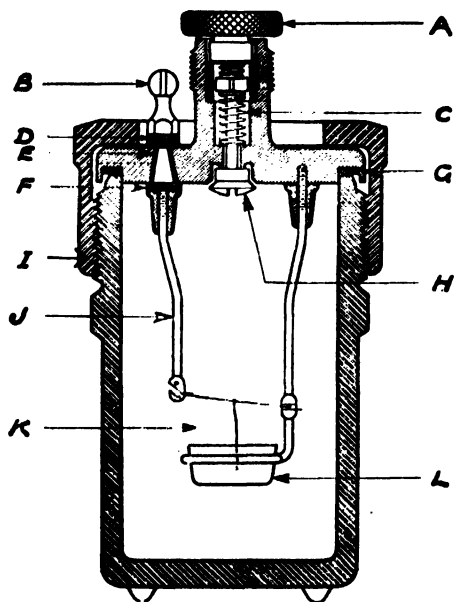


Fig. 2.—DETAILS OF THE ILLIUM OXYGEN BOMB.

A, thumb nut; B, terminal; C, valve spring; D, insulating washer; E, vulcanite sleeve; F, mica washer; G, rubber washer; H, non-return valve; I, octagonal lock nut; J, illium rod; K, wire and cotton fuse; L, capsule.

The Thermometers.

The two thermometers, reading from 14° — 25° C. in $\frac{1}{100}^{\circ}$ C. (thousandths are estimated), readings being made through lenses, one indicating the temperature of the water in the bucket and the other

WEIGHTS OF SUBSTANCES FOR USE IN THE PARR BOMB (340 c.c. Capacity).

TYPE OF SUBSTANCE	SUSPECTED CALORIFIC POWER.		WEIGHT OF SUBSTANCE TO BE TAKEN
	Cals /gm	B Th.U /lb	
Foodstuffs, lignites, bituminous coals and cokes	Up to 7,800	14,000	1 gm
Bituminous coals, semibituminous coals, carbonaceous coals and anthracites	7,800-8,600	14,000-15,500	0.9 gm
Coal tars	8,600-10,000	15,500-18,000	0.8 gm
Fuel oils	10,000-11,500	18,000-20,700	0.6-0.7 gm

that of the jacket, should be as nearly identical as possible.

Adjusting Temperature of Water.

The temperature of the water in the outer jacket can be adjusted at will by admitting either hot or cold water through the jets, and it soon becomes steady, thanks to the four paddles and the rotary pump for forcing water to flow inside the hollow lid. Both the paddles and the pump are on one horizontal shaft, and rotate at about 800 r.p.m.

An arrangement which has been found satisfactory for the supply of hot or cold water is shown in the diagram (Fig. 4 and in Fig. 1A). Motion to the pump and stirrers is supplied via cords by an $\frac{1}{8}$ -h.p. electric motor (1,400 r.p.m.).

Firing the Charge.

For firing the charge a source of electric current (A.C. or D.C.) is

needed. About 10-12 volts from dry cells, accumulators, or a transformer serves. If the mains are used a resistance *must* be employed, and preferably a non-inductive one to avoid burning out the insulation of the bomb terminal. Such a resistance is provided by lamps, and with 100-volt D.C. circuit we use four carbon resistance lamps in parallel, each passing about $\frac{3}{4}$ amp. (see Fig. 1A). This resistance has the additional advantage of showing when the igniting wire has fused.

THE DETERMINATION.

It is important that such a weight of substance shall be used as will be completely burnt; that, in addition to no unburnt carbon, the gaseous products shall contain no carbon monoxide or other unburnt gases. As the result of twelve years' experience in using the Parr bomb (capacity 340 c.c.), we have found that the weights shown in the above table should be used.

The appropriate weight of substance is weighed into the capsule. Solid substances are used in finely powdered, air-dried condition, and, unless very bulky, are not

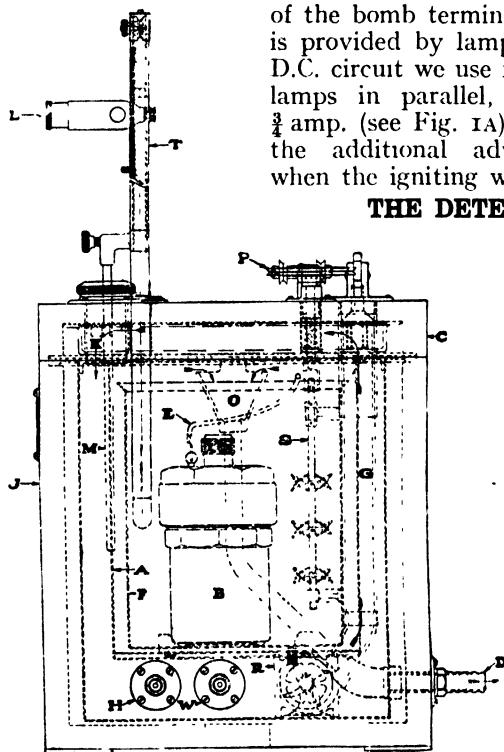


Fig. 3—SECTION THROUGH ADIABATIC BOMB CALORIMETER.

A, inner wall of jacket; B, bomb; C, hollow lid of jacket; D, waste water exit; E, bomb ignition connection; F, oval calorimeter bucket; G, pump delivery tube to lid; H, hot water inlet; J, outer case; K, water return from lid; L, reading lens; M, thermometer safety bar; O, overflow funnel; P, stirrer pulley; R, rotary pump; S, stirrer for bucket; T, thermometer; W, cold water inlet

briquetted. The use of a counter-poised scoop expedites weighing of solids, and an exact number of decigrammes may be taken to facilitate the calculation of the result.

How Liquids Should be Weighed.

Liquids are best weighed directly into the capsule, and it is not worth while to attempt to adjust the weight in this manner. 15-17 drops will usually give a suitable amount. Special precautions are needed with highly volatile liquids such as petrol.

Substances that are Difficult to Ignite.

Substances of high ash content (such as boiler clinkers) and substances of high ignition temperature (such as high-temperature coke) should be intimately mixed with pure sugar in the proportion of 0.5 gm. of substance to 1 gm. of sugar. A clay crucible should be used for the combustion, or the metal capsule lined with ignited asbestos. Allowance should be made for the heat of combustion of the sugar.

The Firing Arrangement.

Taking the bomb lid, 3-4 in. of the thin nichrome wire (36 S.W.G.) is tightly stretched

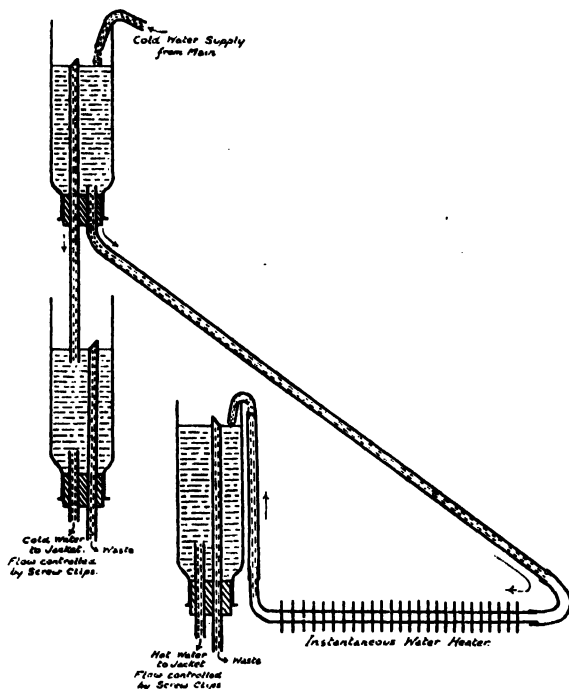


Fig. 4. ARRANGEMENT OF APPARATUS FOR SUPPLYING HOT AND COLD WATER TO CALORIMETER JACKET.

merely breaks in the middle, no correction for its heat of combustion is needed, and no projection of fused metallic oxides on to the walls of the bomb occurs.

Preparing the Bomb.

The bomb, having been rinsed out with distilled water and allowed to drain for a few seconds* (not dried, for the presence of moist oxygen seems necessary for complete combustion), is placed in the socket on the filling bench (see Fig. 5), the lid is put on carefully, and the holding-down screw cap

* If a sulphur determination (see later) is desired also, 5 c.c. of distilled water should be pipetted into the bomb, 5 c.c. being removed from the bucket so as not to alter the water equivalent of the system.

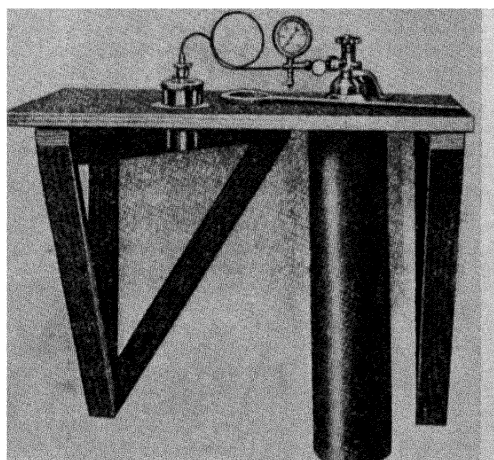


Fig. 5.—THE OXYGEN CONNECTION, WRENCH AND SOCKET FOR BOMB.

screwed down, finishing with the octagonal wrench, excessive tightening not being necessary or advisable, as it tends to destroy the rubber washer without improving the joint. By screwing the hexagonal nut by hand on to the screw thread of the lid, the bomb is put into gas-tight connection with the pressure gauge and oxygen cylinder.

The needle valve of the connector is opened a quarter-turn, and the main valve of the cylinder cautiously opened by tightly holding the middle of the folding key in the left hand and using the right fist as a mallet, so that the pressure rises to about 26 atmospheres in about a minute. Faster filling is more difficult to control and tends to blow the charge out of the capsule.

The main valve is turned off, tightened up, and the oxygen in the connections released by the release valve. After disconnecting the bomb, the non-return valve is held on its seating by screwing on the valve thumb-nut by which the bomb is lifted out of the holder and carried to the calorimeter.

Positioning the Bomb in the Bucket.

The bucket is put into the oval space provided in the water-jacket, care being taken that the notch in the lip is opposite the pointer on the jacket, and the handle folded out of place. The bomb is now positioned in the bucket so that a flat on the octagonal holding-down nut faces the operator (this allows the thermometer bulb to clear the bomb), and so that the terminal is in a convenient position for clipping on the connector. 2,000 ml. of water, at a convenient temperature, 15°-18° C., is measured out to the "D" (deliver) mark of the graduated flask, and poured into the left-hand rear portion of the bucket, completely immersing the bomb.

Any oxygen leakage will now be shown by bubbling, in which case it may be necessary, after releasing the pressure as described later, to fit a new washer. It is dangerous to fire a leaking bomb. The

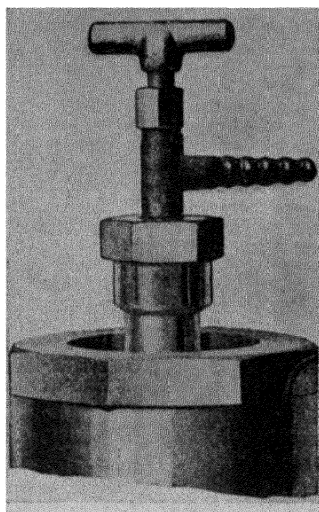


Fig. 6—THE SLOW RELEASE VALVE FOR THE ILLUM BOMB

lid is swung into position, the thermometers lowered, and the motor and consequently the stirrers and pump, set in motion (see Fig. 1A)

The Charge is now Fired.

By admitting either hot or cold water to the jacket the two thermometric readings are made identical, and two to three minutes thereafter the temperature of the calorimeter water is read to 10.00° C and the charge fired, the firing current being shut off by a double-throw switch immediately after firing.

The hot water is turned on as soon as the temperature

of the calorimeter water starts to rise, which it should do in about 15 seconds after firing, otherwise a misfire is to be suspected. The two temperatures are kept as closely together as possible, never differing by over 0.1° C., until after 5 minutes, when, the rise in temperature of the calorimeter water having become very slow, the hot-water feed is shut off. The system is left for another 5 minutes, making 10 minutes in all after firing. (During this waiting period a weighing for the next determination is usually made.) The temperature is again read, and the rise in temperature found.

Allowing for Heat of Combustion of Cotton Thread.

To allow for the heat of combustion of the cotton thread, 0.01° C. is deducted from the observed rise. This gives the true rise which, multiplied by the water equivalent of the calorimetric system, gives the number of calories generated during the combustion with an accuracy sufficient for technical purposes.

Duplicate determinations should agree to within 0.3 per cent., or 0.01° C., for the usual 3° C. rise. Greater accuracy can be secured, but the errors due to sampling, of solid fuels in particular, are much greater than 0.3 per cent.

After stopping the motor, the cold-water supply is turned on to bring down the temperature of the water-jacket, so that it will be about right for the next deter-

mination. A complete determination takes about 20 minutes, and 15 can easily be made in a working day. The bomb is removed from the water, wiped, and the pressure released by giving the valve thumb-nut a turn and pressing with the palm of the hand, after which it may be opened. If desired, the ash residue in the capsule may be weighed as a rough check of the ash content.

Corrections for Nitrogen and Sulphur.

It is only in precise work that these need be applied, for they are nearly always below 1 per cent. of the calorific value, and occasionally fall within the limits of experimental error (0.3 per cent.).

THE DETERMINATION OF SULPHUR BY THE BOMB-WASHING METHOD.

This is the only reliable method for the determination of sulphur in liquid fuels, and is generally satisfactory for all fuels.

5 c.c. of distilled water, to absorb the sulphuric acid formed from the sulphur on combustion with oxygen, is put into the bomb before closing, and 5 c.c. removed from the calorimeter bucket. After the determination of calorific value is finished, the bomb is allowed to stand for 15 to 20 minutes to allow the acid mist to settle. The pressure is very slowly released during 5 minutes by the apparatus shown in the diagram (Fig. 6).

After carefully opening the bomb, the lid and valve (particularly the inside of the valve) are washed first, then the bomb walls and capsule, the washings being received in a 250 c.c. beaker. These washings may be titrated with the standard sodium carbonate, as already described. In the case of coke, mixing with sugar as already described, prevents the formation of sulphur dioxide, which otherwise is liable to occur. 2 c.c. of concentrated HCl is added and the solution boiled, filtered into a 400 c.c. beaker, and the filter paper washed thoroughly with boiling water. The filtrate and washings are heated to boiling and the sulphuric acid precipitated by an excess of 10 per cent. BaCl₂ solution—about 10 c.c. being usually sufficient—the solution is allowed to stand overnight. Next day the precipitate is collected on a 42 Whatman filter paper

or a pad of ashless paper pulp, washed, dried, ignited and weighed.

Weight of sulphur = weight of BaSO₄ × 0.1373.

THE DETERMINATION OF THE WATER EQUIVALENT OF THE CALORIMETRIC SYSTEM.

This involves generating within the bomb (by combustion or electrical means, usually the former as simpler and cheaper) a known amount of heat and measuring the rise in temperature of the system. A number of standard calorimetric substances are available—benzoic acid (6,322 cal./gm.), naphthalene (9,612 cal./gm.) and cane sugar (3,945 cal./gm.)—the last is preferred by the author. Standard samples of benzoic acid can be used when the highest accuracy is desired, but the manipulation is more difficult than with sugar. About the same rise in temperature, namely 3° C., as with an ordinary coal, is aimed at, and for this 1.75 gm. of dry, powdered sugar is weighed out. The combustion, etc., is done exactly as usual. For precise work allowance should be made for the heat of formation of the nitric acid; this might add about 5 to the water equivalent.

CALCULATION OF WATER EQUIVALENT.

Calories generated = 1.75 × 3,945 cal.
from the sugar + 0.006 × 4,000 cal.
from the cotton; i.e., 6,926 cal.

Temperature rise = 2.858° C. (say).

∴ Water Equivalent =

$$\frac{\text{Calories generated}}{\text{Temperature rise } ^\circ\text{C.}} = \frac{6,926}{2.858} = 2,424 \text{ gm.}$$

The water equivalent should be determined over a range of temperature and the mean value taken to eliminate thermometric errors. In all bomb calorimeter work the same thermometer should be used for the readings, kept for that purpose exclusively, and not interchanged with others, for the water equivalent is dependent on the thermometer used.

As a rough check of the water equivalent of the system, all the component parts, bomb, bucket and water, may be weighed, and the sum of the products—Weight × Specific Heat—gives it approximately.

CHEMISTRY IN THE STUDY OF DISEASE

PART I.—A BRIEF OUTLINE OF BIOCHEMISTRY

By SIDNEY L. TOMPSETT, Ph.D.(Glas.), B.Sc.(Lond.), A.I.C.

WITHIN the last 15 years biochemistry has assumed an importance equal to that of the other branches of chemistry. Biochemistry is concerned with the application of chemistry to the study of all living things. The study of the chemical processes taking place in the human organism is divided into physiological and pathological chemistry. The former is concerned with the normal processes and the latter with those in disease. In a short series of articles such as these, only the fringe of pathological chemistry can be touched on. The subject matter to be dealt with will be concerned mostly with industrial diseases

Plant Life.

The human body may be likened to a "natural machine" and, like all machines, requires energy for it to function. Plant life, in contrast to animal life, can utilise the energy of the sun's rays. The plant builds up complex substances, e.g., starch, from such substances as carbon dioxide and water with the aid of this energy. In plant and animal tissues, in the presence of oxygen, these complexes are "burnt," carbon dioxide and water being formed and the energy becoming free and available for the tissues. It will be seen then, that animal life uses the energy of the sun's rays indirectly, plant life being the intermediate.

Animal Life.

The human body, as any machine, has many parts and is in constant need of repair. The tissues in which the "fuel" is burnt are composed chiefly of protein compounds, while the skeleton which forms the supporting structure consists chiefly of calcium phosphate. The decom-

position products of worn out tissues are excreted and these replaced. The human diet consists chiefly of complex carbohydrates, e.g., starch, proteins and fats. The carbohydrates are the chief source of energy and are "burnt" in the tissues in the form of glucose. The proteins are the material from which new tissues are formed, while fat forms another, although less important, source of energy.

DIGESTION.

Carbohydrates, proteins and fats, as present in natural foodstuffs, cannot be absorbed from the intestine, owing to their large molecular weight. Digestion is concerned with the hydrolysis of these substances into small molecules which can pass through the walls of the small intestine into the blood vessels which line it. This hydrolysis, which is produced by a series of enzymes, results in the formation of monosaccharides, amino acids, free fatty acids and glycerol. The nature of the enzymes may be summarised as in the table on page 1197.

During digestion, bile is secreted into the small intestine from the liver via the bile duct. The bile contains bile pigment, a waste product, and bile salts which have the unique property of emulsifying fats in aqueous solution, thus aiding their hydrolysis and absorption. The bile pigments are derived from hæmoglobin, the respiratory pigment of the red blood cells.

In the small intestine, digestion is completed and all absorption takes place. Amino acids and monosaccharides pass into numerous small blood capillaries which line the walls and are carried to the liver in the portal vein. The fatty acids and glycerol enter a series of channels called the lymphatics, which empty into the jugular vein.

TABLE SUMMARISING NATURE OF ENZYMES.

Where Action Takes Place.	Enzymes.	Nature of Action.
Stomach	Pepsin ..	Proteins hydrolysed to proteoses and peptones.
Small Intestine ..	Lipase ..	Fats hydrolysed to free fatty acids and glycerol.
Small Intestine ..	Diastase ..	Starch hydrolysed to maltose.
Small Intestine ..	Trypsin ..	Proteins, proteoses and peptones hydrolysed further.
Small Intestine ..	Erepsin ..	Protein disintegration products hydrolysed to amino acids.
Small Intestine ..	Lactase Maltase Sucrase	Lactose, maltose and sucrose hydrolysed to their respective monosaccharides.

} Present in the pancreatic juice which flows through the pancreatic duct into the small intestine.

} Secreted from the wall of the small intestine.

The contents of the small intestine empty into the large intestine, where much water is absorbed, and then into the rectum where they are known as faeces. During passage through the intestines the bile pigment is reduced to stercobilin, which is identical with urobilin, a pigment found in urine in certain pathological conditions. Some of the stercobilin is absorbed to be re-excreted in the bile as bile pigment.

Blood.

Blood is conveyed over the body by a series of channels known as arteries and veins. In the tissues the arteries subdivide into numerous capillaries through the walls of which nutrient substances and oxygen pass to the cells and waste products returned to the blood. These capillaries then join up to form the veins. Every tissue of the body has its set of arteries, capillaries and veins. Blood is a yellow coloured fluid (known as plasma) with numerous reddish coloured cells suspended in it. These cells contain a substance, hæmoglobin, which is responsible for the carriage of oxygen from the lungs to the tissues. During life, red blood cells are constantly being broken down and new cells formed. The hæmoglobin from broken down cells is converted into bile pigment and excreted in the bile. Freshly drawn blood, if allowed to stand, will clot, but this may be prevented by the addition of 0.1 per cent. potassium oxalate.

The Liver.

The functions of the liver may be summarised as follows:—

1. Secretes bile into the small intestine.
2. Glucose is stored as a polysaccharide, known as glycogen, a substance very similar to starch. This process and its reversal are enzymic. Sugars, such as galactose and fructose, are first converted into glucose before being polymerised to glycogen.
3. During the metabolism of amino acids, ammonia is split off. In the liver ammonia is converted into the neutral, relatively less toxic substance urea.
4. The liver is able to render many substances toxic to the tissues, innocuous by conjugation with sulphuric and glycuronic acids to form ether sulphates and glucuronates. Many drugs and products of intestinal putrefaction are detoxicated in this fashion.

The Metabolism of Carbohydrates, Proteins and Fats.

Carbohydrates are the chief source of energy, but since the body normally receives amino acids in far greater quantity than are required for tissue repair, these can be utilised for this purpose also. The amino group is split off and excreted as urea while the rest of the molecule is converted into glucose. Fat, although a source of energy, is chiefly a storage material. It is oxidised in the body only very slowly and only to completion when

TABLE OF THE MOST IMPORTANT HORMONES AND THEIR ACTION.

Gland Secreted by.	Name of Hormone.	Action.
Islets of Langerhans of the Pancreas.	Insulin ..	Is necessary for the "burning" of glucose in the tissues. When there is a lack of secretion as in diabetes mellitus, the oxidation of glucose is retarded and so collects in the blood and may be excreted in the urine. Under such conditions the oxidation of fat does not proceed to completion and results in the formation of toxic intermediates.
Suprarenals	Adrenaline	Controls the pressure of the blood in the arteries and the rate at which the glycogen of the liver is converted into glucose for use in the tissues
Thyroid	Thyroxine	Controls the <i>rate</i> at which glucose is "burnt" in the tissues.
Parathyroids ..	—	Appears to control the metabolism of calcium. If the glands are removed, the blood calcium is lowered, the animal will develop tetany and die. Injection of the hormone into the blood stream results in the breaking down of bone. This results in an increase of the concentration of calcium in the blood and in the excretion in the urine and faeces. <i>Note</i> —Vitamin D (calciferol) is concerned with the absorption of calcium from the intestine.

plentiful supplies of glucose are being oxidised at the same time. When the oxidation of glucose is impaired, or is absent, the fats are only partially oxidised and certain toxic intermediates, e.g., β -hydroxy-butyric acid, aceto-acetic acid and acetone remain.

Excretion.

Waste products are removed from the body by the:—

1. *Lungs*.—In the lungs the blood passes through capillaries which are separated from the air chambers or alveoli by very thin walls. Oxygen passes from the alveoli into the blood to combine with the hæmoglobin of the red cells. This combination is very unstable and breaks down when the blood enters the tissue capillaries. Carbon dioxide passes from the blood into the alveoli and is expired.

2. *Kidneys*.—The kidneys are responsible for the removal of most of the non-volatile waste material from the body. From certain of the blood capillaries in the kidney, what might be described as an ultrafiltration takes place. The ultrafiltrates are similar in composition to the blood except that they do not contain any protein. The ultrafiltrates pass into and through long narrow tubes which unite and empty into the bladder. During

passage through these tubes, a large amount of water and substances of use to the body are absorbed into other blood capillaries which line the tubes. All the glucose and part of the inorganic salts are absorbed. Waste products, e.g., urea, uric acid, etc., are not re-absorbed. The urine that collects in the bladder represents a concentrated solution of these waste products.

3. *Large Intestine*.—The passage of high concentrations of metals, such as iron and, in certain abnormal cases, lead, mercury, etc., through the kidney would cause permanent damage to this organ. Nature's way of overcoming this difficulty is to excrete them mainly through the walls of the large intestine into the fæces.

Hormones.

The hormones might be described as "animal drugs," and are active in very minute amounts. They are not enzymes, although some of them are thermolabile. From the glands in which they are formed they are secreted into the blood stream. In the body their secretion is very carefully balanced. An under or over secretion of any one of these hormones puts the balance out and the person becomes "ill." A list of the more important hormones and their action is given in the table above.

CHEMISTRY IN CIDER MAKING

PART II.—CHEMICAL CONTROL

By B. T. P. BARKER, M.A.,

Director of the National Fruit and Cider Institute

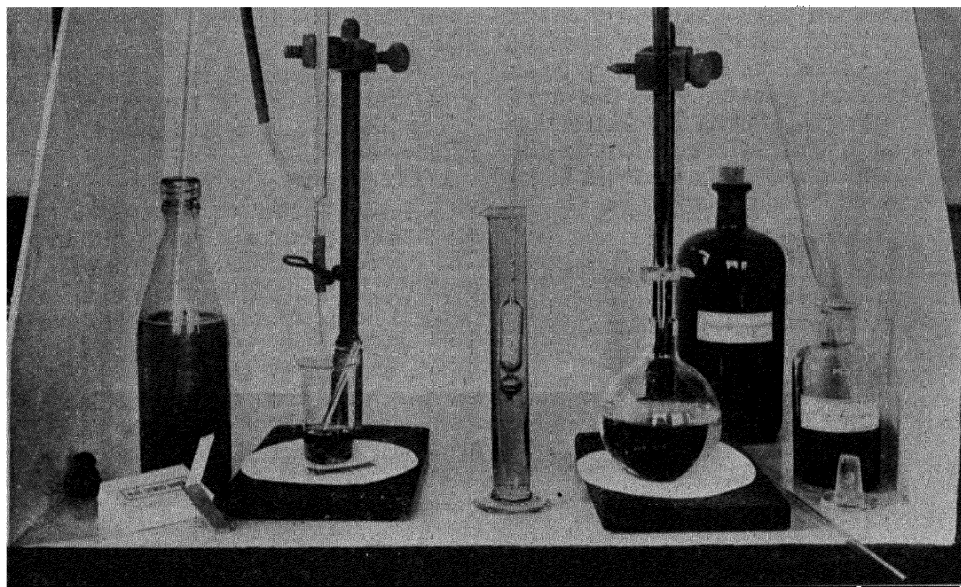


Fig. 1.—APPARATUS REQUIRED FOR ROUTINE ANALYSIS OF CIDER.

Left-hand burette: $N/6.7$ caustic soda for acidity determination. Right-hand burette: 0.0785 per cent. permanganate for tannin estimation. Centre: specific gravity hydrometer.

THE previous account of cider and its methods of manufacture will have indicated already the nature of the chemical control required in the production of the beverage and the examination of samples in respect of soundness and purity. The more detailed account of the methods of examination and analysis now follows.

The chemical work involved is concerned, firstly, with the composition of the juices and ciders in relation to the problems of blending; secondly, with the chemical changes occurring during the preparation of the beverage; thirdly, with the chemistry of the finished product, particularly in relation to abnormal features indicating possible onset of disorders or metallic contamination acquired during the making processes; and fourthly, with tests for

purity and possible sophistication of the beverage.

Routine Analytical Determination.

For purposes of blending juices or ciders the two outstanding natural characters requiring determination are acidity and "tannin" content.

Acidity.

The acidity of a freshly expressed juice is determined by means of a standard solution of sodium hydrate, the strength of which for convenience of subsequent calculation is such that one cubic centimetre is equivalent to 0.01 gm. of malic acid. This is represented by a $\frac{N}{6.7}$ sodium hydrate solution. 10 c.c. of the juice are

titrated with the standard alkali, either blue litmus or brom-thymol paper being used as an external indicator. The indicator cannot be used in liquid form added to the juice, for the brownish colour of the the latter obscures the colour changes of the indicator as titration proceeds and the end point cannot be seen clearly.

Used in this way, the acidity of the juice can be stated direct without calculation from the reading of the volume of alkali solution required for neutralisation of the 10 c.c. of juice. 1 c.c. of the soda solution represents 0.1 per cent. of malic acid in the juice, the total acidity being expressed usually in terms of this acid. Actually other substances of acid reaction as well as malic acid are present in the juice, but their amounts are stated to be small and negligible in comparison.

Total Acidity in Ciders.

The same method is adopted for the estimation of total acidity in ciders. In their case, however, it is necessary to remove completely any dissolved carbon dioxide before titration. This can be done by gentle warming of the liquor, which in that case must be cooled to 60° F. again before being measured out for titration. Alternatively, removal can be effected by thorough agitation of the sample of juice and subsequent filtration through fine filter paper.

"Tannin."

Under this term, so far as apple juices and ciders are concerned, are almost certainly included many substances which are not true tannins as well, possibly, as more than one kind of tannin. These compounds have not been very closely investigated hitherto. As a group they are responsible for certain flavour and colour characters in ciders and the methods of their total quantitative determination have sufficed to provide a fair measure of the degree of concentration of those characters. That from the applied point of view in relation to blending requirements is the main thing: and so long as that is achieved by any individual method of analysis used it has not been regarded as of more than secondary importance which method is adopted, so long as it is used uniformly by the individual analyst, or whether or not the quantitative results represent absolute or only relative amounts

of "tannin." Hence the methods used by different workers differ considerably, both in fundamental features and in details of manipulation.

Method for Ordinary Routine Purposes.

The method used at the National Fruit and Cider Institute, Long Ashton, for ordinary routine purposes is the simplest, but the results it yields are actually the permanganate-reducing powers of the respective juices as estimated in the presence of indigo carmine rather than absolute tannin figures. They include in addition to "tannin" other substances oxidisable by potassium permanganate under the conditions of the method.

The details of this method are as follows:—

1 c.c. cider in 300 c.c. water is mixed with 5 c.c. indigo carmine solution (3 gr. carmine and 50 c.c. H_2SO_4 in 1 litre water). The mixture is titrated with 0.0785 per cent. permanganate until the blue colour changes to green and finally to yellow. The carmine solution is adjusted until 5 c.c. exactly equals 1 c.c. of $KMnO_4$ solution. The end point is indistinct with many ciders, and those with tannin values above 0.4 per cent. should be diluted with water before estimation.

This method admittedly includes in the tannin figure all permanganate-reducing compounds, but gives reproducible results and is some measure of the tannin compounds in a cider. The titration figure minus 1, and divided by 10, gives the "tannin" percentage.

(References: J. Agric. Science 4, Pt. I, 1914 (Spiers). Korner and Nierenstein, Chem. Zeit. 36, 31, 1911 (casein method)).

American workers use a permanganate titration before and after removal of true tannin by a variety of absorbing agents (e.g. bone black). This true figure is generally about 30 per cent. less than the total "tannin" percentage.

(Reference: J.A.O.A.C. p. 141, 50.)

It is also possible to estimate the permanganate-reducing power of a cider before and after fining with gelatine, which precipitates the tannin.

Warcollier, the French cider expert, recommends the method of Manceau, whereby the tannin is removed by catgut and permanganate values obtained before and after. The standard used is pure gallotannin.

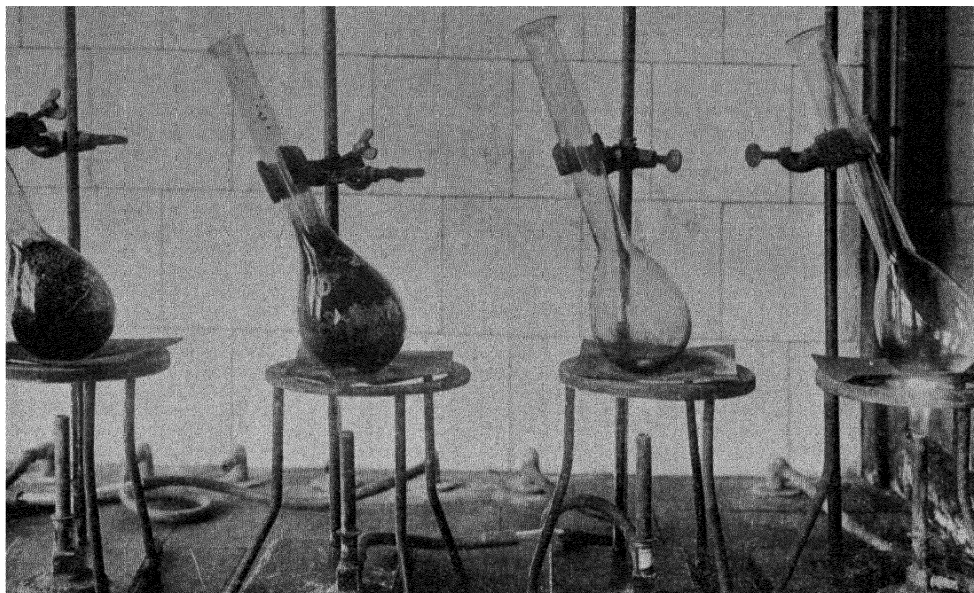


Fig. 2.—DETERMINATION OF TOTAL NITROGEN IN CIDER (1).

The cider is evaporated to a syrup and, after digestion in the normal Kjeldahl method as shown, the ammonia is distilled off and the amount present determined by collection in N_{10} acid with subsequent determination of the quantity of acid neutralised.

Other Estimations Required.

Estimations of the following points are required from time to time in connection with the management of the fermentation of apple juice and the character of the resultant cider: specific gravity, sugar, total nitrogen, pectin and alcohol contents and volatile acidity.

Specific Gravity.

The specific gravity of apple juice and cider is generally determined by means of a hydrometer which is graduated to show the degrees of specific gravity between 1.000 and 1.100. That range normally suffices for all purposes where cider is concerned. The hydrometer reading needs a temperature correction to 15.5°C . if the liquid does not stand at that temperature at the time it is taken. The specific gravity can also be determined by the use of the specific gravity bottle.

The specific gravity of the liquor indicates approximately, as mentioned in the earlier part of this article, the total solids and sugar content of the liquid. A fairly accurate estimate of the amount of solid matter in freshly expressed apple juice can be obtained by the following formula:

$(\text{Sp. Gr.} \times 234) - 234$. For example, if the specific gravity is 1.050, that figure multiplied by 234 = 245.7. On deduction of 234 from this, the result is 11.7, which the results of solid matter determinations with many juices made by the method described in the next section show to be a fairly accurate average approximation.

Total Soluble Solid Matter (Dry Extract).

This determination is made by evaporating in a flat platinum dish 5.5 c.m. in diameter by 2.5 c.m. deep 20 c.c. of the juice or cider on a water bath for 6 hours. This method is the one used by Warcollier. It is difficult to arrive at a constant weight in such determinations; hence the results are expressed by the use of a standard method carried out for a fixed rate of time at a temperature of 100°C .

Reducing Sugars.

The cider tested is first clarified by the use of lead acetate and the excess of the latter removed with one of the appropriate chemicals. The clear liquor is then titrated with Fehling's solution by Lane and Eynon's method or treated gravimetrically by one or other of the numerous modifications of the copper oxide method.

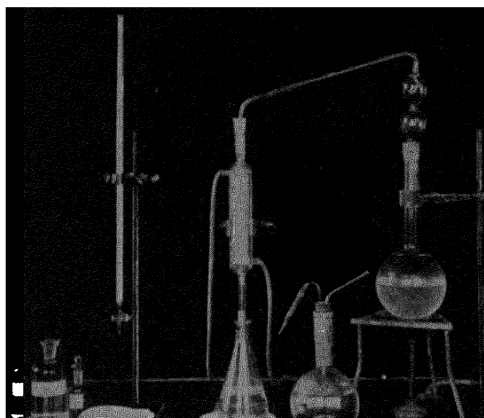


Fig 3—DETERMINATION OF TOTAL NITROGEN
IN CIDER (2)
Showing the distillation of ammonia

Sucrose.

The cleared liquor referred to in the previous paragraph is treated with 10 per cent. citric acid at 100° C. for 15 minutes to secure inversion of the sucrose; or this may be accomplished by adding 2.5 c.c. of a 10 per cent solution of hydrochloric acid to 100 c.c. of the cleared liquor. The flask in the latter case is agitated in a boiling water bath for 5 minutes. The amount of reducing sugar present after inversion is then determined by one of the methods referred to under that head and the difference between the figure so obtained and that already obtained for the reducing sugar multiplied by 0.95 gives the percentage of sucrose.

Non-Sugar Extract.

The amount of the material classed under this head is obtained by subtracting from the dry extract figure the sum of the reducing sugars and sucrose less 1 gm.

Nitrogen.

The nitrogenous compounds present in apple juice and cider are almost entirely organic nitrogenous substances belonging to the classes of albuminoids, amides and amino acids. Usually no attempt is made to determine the individual quantities of the compounds of these respective classes present, the figure for total nitrogen normally being sufficient for ordinary requirements.

The juice or cider is evaporated to a syrup *in vacuo* or under ordinary pressure

with 20 c.c. of concentrated sulphuric acid per 150 c.c. of cider. The latter is a convenient quantity to use. After digestion according to the normal Kjeldahl method, the ammonia is distilled off and the amount present determined by collection in $\frac{N}{10}$ acid with subsequent determination of the quantity of acid neutralised. From the data thus obtained the quantity of nitrogen in the sample of cider can be calculated exactly.

Pectin.

The older method of pectin determination in which the cider is concentrated by evaporation to a small bulk and then precipitated with excess of alcohol has recently been found to be less satisfactory than the following method, which is the calcium pectate method of Carré and Haynes. The latter has been found to be very reliable and to give consistent results, both with freshly expressed juices and juices in the early stages of fermentation.

The juice is first neutralised and then 100 c.c. $\frac{N}{10}$ sodium hydrate solution is added. After 12 hours standing, 50 c.c. each of acetic acid and calcium chloride solution are added. This treatment results in the precipitation of the pectin compounds in the form of calcium pectate, which is filtered off and washed thoroughly and weighed.

As mentioned earlier in this article, the pectin constituents of the fresh juice disappear very rapidly during the course of fermentation and thus dry ciders give, ordinarily, no precipitate with either of the above methods.

Juices and ciders in the earlier stages of fermentation when tested by the alcohol method give precipitates which include some non-pectin material. Consequently, the pectin figure under this method in such cases must be regarded as slightly too high.

Alcohol.

The alcohol in a cider is estimated by taking 100 c.c. of the liquor and adding to it a small amount of carbonate of lime sufficient to neutralise all acidity. After this treatment it is distilled and about 70 c.c. of the distillate is collected. The volume of the distillate so collected is

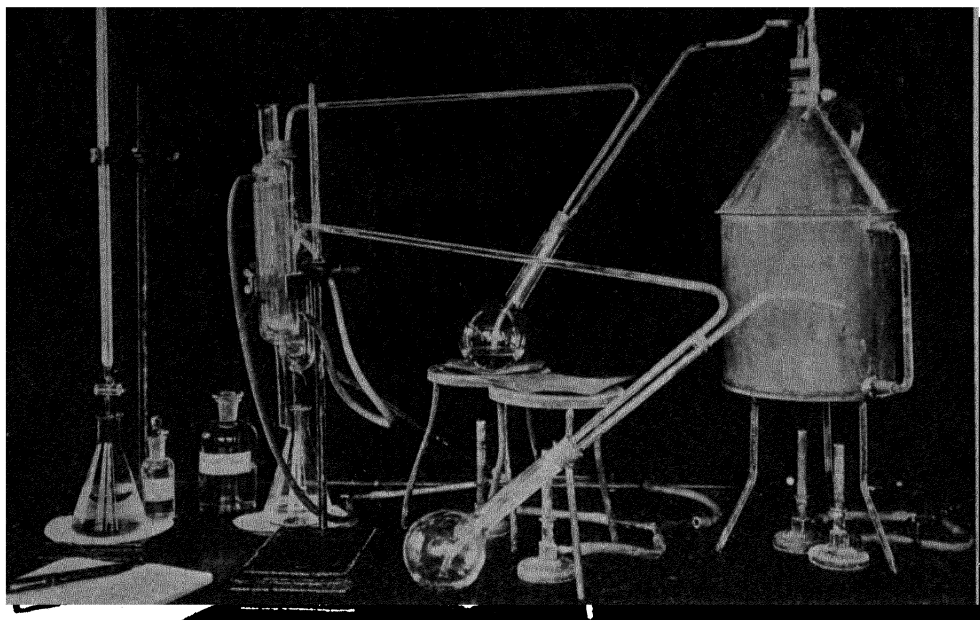


Fig. 4.—DETERMINATION OF VOLATILE ACIDITY IN CIDER.

50 c.c. of the cider from which all carbon dioxide has been removed by gentle warming is subjected to steam distillation.

then made up to 100 c.c. and the temperature brought to 15.5° C. The specific gravity of the distillate is then determined by direct weighing in a specific gravity bottle. From the specific gravity so ascertained the percentage of alcohol present is found by reference to the well-known tables showing the relations between specific gravity and percentages of alcohol both by weight and by volume.

Volatile Acidity.

Various methods for the determination of volatile acidities in ciders have been tested and the following has been found satisfactory for routine work. 50 c.c. of the cider, from which all carbon dioxide has been removed by gentle warming or slight agitation, is subjected to steam distillation. Suitable precautions must be taken during this operation to ensure that there is no chance of any mechanical transference of fixed acids from the distillation flask to the receiver. Distillation is continued until 300 c.c. of distillate is collected. A titration of the latter with $\frac{N}{10}$ sodium hydrate solution in a flask is then made. For calculation purposes

1 c.c. $\frac{N}{10}$ sodium hydrate solution
= 0.006 gm. acetic acid.

The volatile acidity is normally stated in terms of acetic acid, although various other volatile acids such as caprylic and caproic are present in small quantities.

Special Determination for Abnormalities.

Occasions arise from time to time when it becomes necessary to make special determinations which have reference to possible abnormal features which may be associated with a particular juice or cider. Amongst these cases may be included the results of various disorders in cider and metallic contamination acquired during some stage or other of the cider-making processes.

Acetification.

With regard to the special chemical features presented by cider affected with the various disorders which have already been referred to, in the case of acetified ciders the determination of volatile acidity will generally suffice to indicate the extent of the trouble. The volatile acidity of a cider which can be considered as sound and reasonably free from undue acetification should not exceed 0.2 per cent.

Ciders possessing a volatile acidity materially higher than this must be considered as having an undue amount of acetification.

Detection of "Cider Sickness."

The presence of the disorder of "cider sickness" can be detected readily by the characteristic alteration in smell and flavour, particularly in conjunction with a very low specific gravity figure. After a considerable period of standing, affected ciders tend to lose the characteristic aroma and flavour of "sickness" and the following test for the presence of formaldehyde, if it gives a marked positive result, can generally indicate if a cider has been at some earlier stage affected by this disorder.

To 10 c.c. of liquid to be tested add 2 c.c. of a 1 per cent. solution of phenylhydrazine-hydrochloride, freshly made up, and filtered, and then 1 c.c. of fresh 5 per cent. solution of potassium ferricyanide and finally 5 c.c. of concentrated hydrochloric acid. A brilliant magenta-like colour is formed if formaldehyde is present.

Ropiness and Oiliness.

The disorder of ropiness and oiliness requires no special chemical examination, since the presence of the disorder is obvious to the eye by the oily or mucilaginous character of the liquor.

Blackening Disorder.

Ciders subject to the blackening disorder can be recognised even before blackening has actually taken place by the determination of iron content in the ash, the amount of iron in such cases being abnormally high.

Metallic Contaminations.

Metallic contaminations of other kinds can also be determined by an examination of the ash.

Ash Determination.

The determination of the total ash in apple juice and cider requires considerable care on account of the difficulty of removing the carbon or the organic matter completely. The following method may be recommended:—

100 c.c. of cider is evaporated to dryness in a gold basin or a porcelain

dish of good quality. The dry matter in the dish is then subjected to somewhat greater heat to burn off the carbon of the organic matter. If the carbon is not satisfactorily burnt off completely during this operation the charred mass in the basin should be leached with hot water three times and reheated. The ultimate residue is then strongly heated and, when a white or greyish-white ash is secured, the leachings referred to in the previous sentence transferred to the dish and gently dried off. The weight of the total ash is then determined and the figure as obtained is taken as "carbonate ash."

The ash so obtained can then be examined in the usual ways for its various mineral constituents. As a preliminary to this the "carbonate ash" requires conversion to "chloride ash," which is accomplished by the addition of 1 or 2 c.c. of A R hydrochloric acid, re-drying and weighing for chlorides. It is then dissolved in hot water, the solution made up to 100 c.c. and used for the required estimations.

Determination of Individual Constituents of the Ash.

The individual constituents of the ash which particularly require determination on occasion are potassium, calcium, lead, copper, tin, iron and phosphoric acid.

(a) *Potassium*.—This is usually estimated in cider ash solutions by the perchlorate method.

(b) *Calcium*.—This element is precipitated as oxalate and a determination by titration with permanganate in the usual manner made.

(c) *Lead*.—Since it is rare that this element occurs in the ash except in minute quantity, the colorimetric method of determination as lead sulphide is suitable.

(d) *Copper*.—The copper content is determined by matching the depth of colour obtained on addition of sodium diethyl-dithiocarbamate to a measured volume of the ash solution from which iron and other constituents have been removed by precipitation with excess ammonia. This test gives a brown colour with copper and its sensitivity is such that one part of copper in 100,000,000 parts of solution may be indicated.

(e) *Tin*.—The test for tin recommended is that of Schryver. Tin in the stannous

condition is acted upon by α -dinitrophenylamine sulphoxide in $\frac{N}{10}$ sodium hydrate solution. Under the further procedure mentioned below a violet colour is formed, which reaches maximum intensity on the addition of 1 drop of dilute ferric chloride solution. This test is extremely delicate.

The following is the procedure adopted: An aliquot of the ash solution is made strongly acid with hydrochloric acid and received in a large 1-in. diameter boiling tube closed with a cork, fitted with two glass tubes, one of which is arranged to be 1 in. above the solution. Carbon dioxide is passed through the tube and the contents boiled. 0.75 gm. of pure zinc is quickly added, and when solution is complete, all the tin being in the stannous condition, 2 c.c. of a solution of α -dinitrophenylamine sulphoxide in $\frac{N}{10}$ caustic soda is added. The contents of the test tube are again boiled, and on cooling made up to 100 c.c.

(f) *Iron*.—This element is conveniently determined colorimetrically as sulphonylate.

(g) *Phosphoric Acid*.—Neumann's method is usually adopted for the determination of P_2O_5 . The latter is precipitated in the form of the canary-yellow ammonium molybdate. The precipitate is washed free from acid with sodium citrate and then dissolved in excess soda, after which the excess soda is back titrated with standard acid. The amount of soda neutralised indicates the weight of phosphoric acid present according to the following equation: 1 c.c. $\frac{N}{10}$ sodium hydrate solution = 0.0003004 gm. P_2O_5 .

Tests for Purity.

These are mainly in connection with the addition of sugar or other sweetening agents, the use of preservatives and the addition of acids or other flavouring substances. Many of the possible points arising can be determined by the analytical data obtained by the use of several of the methods already given above.

One determination which is necessary to arrive at an estimate of the amount of dilution or the addition of sugar to a cider is that of original gravity.

Original Gravity.

The cider is brought to 15.5° C. and 100 c.c. slowly distilled until about 80 c.c. have been collected. The specific gravities of the distillate and residue are determined, and from the former is obtained the "spirit indication." By table, this is converted to "degrees of gravity lost" and added to the gravity of the residue. The method is adapted from the official method for beer and has been shown to be satisfactory for cider.

Results agreeing closely with the official method may be obtained by determining the alcohol (by weight) in the cider, and multiplying this by 9.4. The quotient is added to the gravity of the cider at the time of analysis.

Presence of Apple Juice.

From time to time beverages have been sold under the name of cider although not prepared from apple juice. The following test indicates the presence of as small a quantity as 1 part of apple juice in 500 of the liquor.

The sample of liquor is shaken in a test tube with ethyl acetate for a few minutes and the ethyl acetate extract allowed to separate from the "cider" by standing and subsequent decantation. A few c.c. of this extract are then poured down the side of a test tube containing about 10 c.c. of lime water, care being taken that the liquids do not mix. At their point of junction a bright canary yellow colour appears instantaneously if apple juice is present in the sample under examination.

Presence of Sulphur Dioxide.

The only permissible preservative is sulphur dioxide, for the determination of which either the Monier Williams' distillation method or the following method can be used.

50 c.c. of cider is well shaken for 15 minutes with 25 c.c. of a 5.6 per cent. caustic potash solution. 10 c.c. of sulphuric acid of 1:3 strength are added and the acidified mixture then titrated with $\frac{N}{50}$ iodine solution, using starch as an indicator. The following equation is used to show the amount of sulphur dioxide present:—

$$1 \text{ c.c. } \frac{N}{50} I_2 = 0.64 \text{ mg. sulphur dioxide.}$$

THE HIDE AND BONE GLUE INDUSTRIES

By R. BARRY DREW, F.I.C.,

Chief Chemist to British Glues and Chemicals, Ltd.

THE familiar cake glue of commerce finds many uses in industry, not only in the joining of wood, an art which dates from antiquity, but in the manufacture of paper, cardboard boxes, leather goods, matches, calsomins and paints, metal refining and to a lesser degree in a very large number of other industries.

Indeed, in the adhesive field, cake glue is now to a certain extent replaced by other materials—some of animal origin such as fish glue, casein glue, blood, some of vegetable origin such as starch, gum and dextrin, and more recently by synthetic materials derived from phenol or cellulose.

However, the manufacture, testing and employment of these alternative adhesives differ in many respects from cake glue practice, and it is, therefore, convenient for this article to limit ourselves to the description of the Hide and Bone Glue Industry.

Raw Materials.

The raw materials are the hides and bones of animals, chiefly cattle. These are obtained from the fellmonger, the tanner and the butcher.

Principles of Manufacture.

The raw materials contain nitrogenous constituents called scleroproteins which by the action of steam or hot water become changed to a substance (glue) which is soluble in hot water to form a viscous solution that sets to a jelly on cooling. The aim of glue manufacture from hide or bone is twofold. First, the non-glue forming materials (fat, blood, mineral matter) must be separated; second, the glue-forming matter, i.e., the scleroprotein, must be changed into glue by the action of steam or hot water.

Collagen and Ossein.

The glue-forming material in hide is called collagen, in bone, ossein. These two substances are very similar. They are fibrous materials which are insoluble in water though they will swell without dissolving in dilute acids or alkalis.

By long boiling with hot acid or alkaline solution they dissolve and are changed to very simple soluble crystalline substances, the amino acids, the simplest of which is glycine or amino-acetic acid.

At one extreme, therefore, we have an insoluble fibrous material; at the other extreme, a simple soluble acid. Between these two extremes it is possible to obtain a half-way stage—the fibrous material broken down sufficiently to be soluble in hot water but not so far as to be soluble in cold water. This half-way stage corresponds to gelatine or glue according to the extent to which it is carried.

Gelatine and Glue.

When the collagen or ossein is only lightly attacked by hot water it forms a solution which is very viscous and sets to a firm jelly on cooling. This is the gelatine stage. If the action of the hot water is prolonged, or if high pressure steam is used, the product forms a less viscous solution which sets to a weaker jelly—this is the glue stage. Gelatine and glue are, therefore, made from the same type of raw materials and differ in degree rather than in kind. Gelatine has a higher viscosity and jelly strength than glue. There is another important practical distinction, for actually gelatine is made from specially selected raw materials because the purposes (photographic, food-stuffs) to which it is put demand freedom from impurities and colour. For such purposes glue would not be suitable, but

on the other hand, gelatine would be equally unsuitable for many of the purposes for which glue is used, e.g., joinery, distempers, etc.

Hide Glue Manufacture.

The hide pieces, trimmings and shavings, are first washed to remove blood and salt. They are next immersed in milk of lime for a considerable period up to six weeks. The lime swells the hide, dissolves out certain impurities, loosens the hair and changes some of the fat to lime soap. The degree to which the liming is carried out influences the subsequent properties of the glue.

The hide pieces are then removed from the lime bath, washed and immersed in dilute mineral acid, e.g., hydrochloric acid in order to dissolve out any residual lime. The acidified hide is then re-washed till quite free of acid, placed in wooden vats and covered with water.

The Vats.

These vats, usually called pans, are fitted with steam coils so that the water can be heated to any desired temperature. The first heating is usually 80° C. for 8 hours, by which time the outside portions of the hide have dissolved in the hot water. The liquor is then run off to a tank (any fat is skimmed off the top), it is filtered and then evaporated under a vacuum. The evaporated liquor which will now contain about 20 parts glue per 100 of water is bleached, for example, with hydrogen peroxide and run into coolers—long galvanised vessels placed in a bath of running water. In a few hours the liquor sets to a jelly.

The next step is to remove the jelly en bloc and pass it through a slicing machine so that a number of slabs of jelly (usually about $\frac{3}{4}$ -in. thick) are obtained. These slabs are transferred to wire or string nets and placed in a tunnel to dry. The tunnel is about 80 ft. long, 8 ft. high and 6 ft. wide and hot air is blown through it by means of a powerful fan. It takes 2 to 4 days to dry the cakes from a jelly to hard glue. The glue cakes are then removed from the tunnel, graded and packed in bags or barrels.

Returning now to the melting out stage, after the first liquor is run off the hides are covered again with fresh water which is heated up to a higher temperature and this

liquor is run off. A third and fourth liquor is subsequently obtained by which time all the glue-forming matter has been attacked and only a residue of elastin and lime soap is left. This residue, called scutch, is sold as a fertiliser. The total time of melting out is about two days.

Bone Glue Manufacture.

The extraction of glue from bones proceeds along rather different lines, because the glue-forming material (ossein) is intimately associated with mineral matter in the bone. It is not possible to open up the material by swelling in lime water as with hide, and recourse must be had to attacking the bone with high-pressure steam in autoclaves.

The bones on receipt at the factory are picked over to remove meat and other foreign matter which is not glue-forming, such as hoof and horn. They are then crushed to about 1-in. and conveyed mechanically to an extractor. This is a vessel holding 7-12 tons of bones with tight-closing doors fitted with arrangements for passing benzine vapour over the crushed bones—it is in effect a huge dry-cleaning machine.

What the Benzine Does.

The function of the benzine is to dissolve the fat out of the bones (it is only held mechanically), leaving a dry fat free material. The operation takes about 24 hours. This procedure is found to be superior to skimming the fat from the glue liquors as is done in hide glue manufacture. The degreased bone is then conveyed to a rotating sieve (called a polisher) which breaks up the clusters, rounds the edges of the bony fragments and shakes out the dust. From thence the bones are conveyed to the glue department.

The first step is a soaking in water or SO_2 solution to remove soluble substances such as salt. The bones are then packed into an autoclave and submitted to alternations of high pressure steam (30 lbs.) and hot water. The steam softens the bone and changes the ossein into a stage where it is soluble in the later hot water. It takes a dozen applications of steam and water to get all the glue out of the bones, because the action is essentially at the surface and a portion of glue must be dissolved out before the bone underneath can be attacked.

In order to economise water (and for other good reasons) it is usual to work several autoclaves in series, i.e., the effluent from one is used as the feed in for the next. The whole operation of degluing takes about 24 hours. The residue left in the autoclaves is the original inorganic matter of the bone. It is removed, dried, and sold as a phosphatic fertiliser.

Treatment of Glue Liquors.

The glue liquors (which will vary in concentration from 5 to 10 per cent.) are treated with SO_2 gas to lighten and bleach them and passed to a vacuum evaporator which concentrates them to about 40 per cent. This strong liquor is cast in coolers, cut, and dried in a tunnel in the same way as hide glue.

It must be understood that although the majority of the glue made in this country is marketed as cake glue, there are certain other forms such as ground glue, also called size, made by grinding cake glue, pearl glue, which is similar to ground glue, but in a more attractive form, jelly glue (or jelly size) which is essentially the product obtained before cutting and drying. All these variations are produced to suit commercial requirements, but they are in a sense, the same as cake glue and the analytical tests to be described apply equally to all of them.

GRADING AND ANALYSIS.

The glue maker may alter the properties of his glue to a very considerable extent in order to supply the customer with the exact grade he needs. In particular the consistency of the glue may be varied by alterations in the time and temperature of the melting out. As a result there are on the market glues of varying properties and it is, therefore, necessary to provide, for the guidance of consumers, some method of grading.

In the past, the situation was adequately met by reference to the origin of the material, e.g., hide glue or bone glue, by particular description, e.g., joiners' glue, match-making glue, or by the provision of a trade name, usually stamped or moulded on the cake. Thus we have such names as Trumpet Medal Glue, Cathedral Medal Glue (the word "medal" refers to the embossed seal or medallion), and it was the aim of the manufacturers

to ensure that the quality of a particular brand never varied. The problem became more difficult as the use of powdered glue increased, and it became increasingly necessary to rely on analysis.

Analysis of Glue.

The suitability of glue for a particular purpose depends rather on its physical than its chemical properties and, therefore, a purely chemical analysis, such as one would carry out for salt or sugar, is not of great service. As a result of long experience, the trade has developed a number of physical tests which, supplemented by some simple chemical ones, are sufficient to provide information on the behaviour of the glue in practice.

The position at the moment is that two samples of glue may be regarded as matched if they agree in these tests. The method of carrying out these tests has recently been agreed by the trade in collaboration with the B.S.I. and the draft proposals are available to the public (B.S.I.—British Standards Institution, 28, Victoria Street, S.W. 1).

They may be divided into three categories —

(a) Physical tests which indicate the colloidal properties of the glue ;

(b) Chemical tests to determine the proportion of minor constituents, such as salt, SO_2 ;

(c) Special tests such as keeping quality, joint strength.

Physical Tests.

The colloidal properties of the glue, i.e., the extent to which the parent protein has been broken down is reflected in the viscosity, the jelly strength and the melting point. Methods for carrying out these determinations have been agreed and a general parallelism may be noted. Thus a glue of high viscosity will be high in jelly strength and melting point, and a glue of low viscosity will be low in jelly strength and melting point, but the agreement is not very close. Thus, two glues of different make may agree exactly in jelly strength, but may vary several units in viscosity.

Determination of Viscosity.

In all the physical tests extreme care must be exercised in order to obtain reproducible results. The following instructions (taken from the Agreed Methods)

should be followed in minute detail, especially as regards times and temperatures. For the most used range of glues, the B.S.I. Viscometer No. 2 is suitable. It may be purchased from apparatus suppliers and graduated by the analyst himself with cane sugar solution or by the N.P.L., for a standard fee.

"15.00 grm. of the powdered sample is placed in a corked bottle or flask and 85 ml. of cold distilled water added. The flask is allowed to stand for 2 hours and then is placed in a water bath maintained at exactly 65° C. for 10 minutes. Dissolution is aided by gentle stirring or by shaking the flask. The solution is kept for half an hour at 40° C. + or - .05° C. It is then transferred by means of a funnel loosely plugged with cotton wool into the viscometer for testing.

The instrument used is the British Standard U Tube Viscometer (B.S.S. No. 188—1929) standardised in centipoises. It is essential that the time of efflux should be within the accurate range of the instrument chosen which will be usually No. 2 or No. 3 and that the instructions given in the specification are adhered to.

The results are expressed as the viscosity in centipoises of the glue or gelatine at a concentration of 15 per cent. w/w. and temperature of 40° C."

This test is a very suitable preliminary when examining an unknown glue, for by reference to the following table it will be possible for the analyst to "place" the glue.

Comparison of Commercial Glues.

	Relative	
	C.P.	J.S.
Lowest Grade Bone Glue.	6.79	1
	7.07	2
	8.64	3
	9.54	4
	19.17	5
Upper Grade Hide Glues.	22.50	6

Determination of Jelly Strength.

Special and costly apparatus is necessary to obtain jelly strength figures which are reproducible in other laboratories, and it is, therefore, customary for simple relative methods to be adopted.

Where there is a standard glue agreed between customer and manufacturer, the determination of jelly strength is simply

relative and should be carried out in the following manner.

Both the standard and the glue under test are prepared at the same time and in exactly the same way.

A quantity of the sample from 5 to 10 gm. according to the grade, is carefully weighed into a beaker of 150 ml. capacity, and exactly 50 ml. of cold distilled water added from a pipette. A watch-glass is placed over the beaker and the glue allowed to soak all night. In the summer time, when the temperature is between 15° and 22° C. one may, if desired, leave for four hours only. The beaker is then heated on the water bath for exactly ten minutes, care being taken by adjusting the gas that the temperature of the glue does not rise above 60° C.

During this operation, the glue is constantly stirred so that it is all dissolved in the time, which may be ascertained by lifting up the beaker and glancing through the bottom where the thick glue tends to remain. The glue or liquor is immediately poured into an aluminium or porcelain cup and after two minutes the lid is put on. The cup is left overnight in a room where the temperature is between 16° and 20° C.—preferably in a thermostat at 15° C., or in a bath of running cold water—and the next morning, the lid is removed and the jelly compared against the unknown by pressure with the finger.

Instead of the finger any accurate type of instrument may be used, provided there is previous agreement on the concentration and temperature to be used.

When there is no agreed standard glue for comparison, it is recommended that the Bloom jelly strength tester ('Industrial and Engineering Chemistry,' Analytical Edition, 1930, p. 348) is used in the manner detailed therein."

Determination of Melting Point.

The determination of melting point is less often necessary and reference may be made to the B.S.I. compilation :

"All methods for the determination of melting point are approximate. The Cam-bon apparatus is recommended to be used as follows :—

The apparatus consists of a hollow, truncated brass cone 22 mm. in height, 17 mm. external diameter at top, 15 mm. external diameter at bottom. Its thick-

ness is such that the weight is exactly 7 gm.

Into this fits loosely a glass rod 40 mm. long, 3 mm. diameter, which is flattened at one end to a disc 9 mm. thick and fashioned at the other end into a hook.

20 gm. of the powdered sample is placed in a beaker and 80 ml. distilled water added. The beaker is allowed to stand at least 2 hours and then is placed in a water bath and maintained at 50° C. for 10 minutes. Dissolution is aided by gentle stirring. The liquor is poured into the bowl and the rod inserted and maintained in an upright position overnight for the jelly to set. The apparatus is then suspended in a beaker of water at 15° C., the beaker placed in a water bath at 20° C. and the water in the latter slowly heated ($\frac{1}{4}$ ° C. per minute) until the bowl falls off from the rod. The temperature of the water in the beaker when this occurs is taken as the melting point of the substance."

Chemical Tests.

Chemical tests are only necessary for special purposes, for example, a determination of the SO₂ content may become advisable if the glue is to be used as an adhesive for coloured papers, or an analysis for salt content if it is intended to stick aluminium foil, or the pH test if one requires a neutral glue. The methods of carrying out these tests are all described in the above-mentioned reference and it is sufficient for this article to reproduce the pH test.

The pH Test.

"1 gm. of glue is dissolved in a small quantity of warm recently boiled distilled water in a stoppered flask of chemically resistant glass and the volume made up to 100 ml. with recently boiled and cooled distilled water. After shaking and allowing to cool to ordinary temperature, the pH value of the solution is determined. Care shall be taken throughout the operation to avoid absorption of carbon-dioxide from the air. The Michaelis Indicators with Hellige or Lovibond comparator may be used but in the event of any disagreement in the pH value, this must finally be determined by actual measurements of the potential by a recognised method, e.g., the glass electrode or quinhydrone cell."

Special Tests.

Of these the most used are colour and odour and usually with reference to an agreed standard. For the odour test it is convenient to soak the sample in cold distilled water and then note the odour before and after heating on the steam bath.

Keeping Quality.

Keeping quality or the resistance of the sample to infection is always a very important determination because, as will be shown later, bacterial degradation is a common source of trouble in the use of glue. The test is carried out as follows:—

"6 gm. of glue is soaked in 20 ml. of distilled water, taken up on a water bath and poured into a Petri dish 3-in. diameter. The Petri dish is covered and placed in an incubator maintained at a temperature of 40° C. After each 24 hours the Petri dish is taken out of the incubator and allowed to cool before inspection. The periods are noted when liquefaction, putrefaction or moulds occur."

Joint strength is of importance only for wood work and needs special skill and apparatus. The method is described in B.S.I. Specification 3 V.11 and also in the compilation mentioned above. There are many other tests that have been developed for special purposes, e.g., the alum test for glue intended for sizing, etc., the foam test for glue to be used in machines, but all these are too specialised for description here.

To summarise, the duty of an analyst in a factory using glue is generally limited to a comparison test of jelly or viscosity against an agreed standard and supplemented by special tests directed to the purposes to which the glue is to be put.

Use of Glue.

With certain exceptions, such as the preparation of dry distempers, glue is used in hot, strong solutions. The art of dissolving glue is not difficult, provided two rules are borne in mind, namely, to avoid heat damage and to avoid putrefaction.

Dissolving Glue.

The glue (be it in cake, powder or pearl form) is first allowed to soak in the requisite proportion of cold, clear water until completely swollen. Ordinary galvanised buckets are very suitable. They should

be thoroughly clean. This operation takes from 2 to 12 hours, according to the physical type of the glue. The swollen glue is then transferred to a water jacketed vessel, preferably of tinned copper or stainless steel, and heated with hand or mechanical stirring till a temperature of 60° C. is attained. The glue liquor is then ready for use.

Simple as the procedure is, any attempts to deviate from it will cause troubles. If the soaking water is not cold, the glue will not swell and subsequent melting will be difficult, lumps being formed; if it is not clean, the glue may become infected and later smell. If the temperature in the water bath be carried above 60° C., there is an increasing tendency to form scum, to lower viscosity and to deepen the colour. Admittedly it is possible to melt glue direct in hot water but only when the glue is finely powdered and special mechanical stirrers are used.

Making a Strong Solution of Cake Glue.

A problem arises when it is desired to make a strong solution say 1 : 1 of cake glue. To put equal weights of cake and water in a vessel would not be satisfactory as the water would not cover the cakes of glue. In this case, one leaves the glue soaking in excess of water until it has soaked up the required amount. This can be judged by pouring off the supernatant water and weighing the moist glue. More simply after some experience it is possible to judge by time alone. After the water is poured off the moist cakes are covered with a damp bag and left to mature—a matter of several hours—until the moisture is evenly diffused through the cake. It is then possible to melt up in a water-jacketed vessel as usual.

Glue liquors are always liable to heat degradation even at such a medium temperature as 60° C., and it is, therefore, preferable to make up enough only at most for a day's supply. It is customary in larger factories to make up two or more batches of liquor per day and transfer from time to time portions to the machines or to small glue pots if it is a case of hand gluing.

These glue pots are often made of stainless steel and electrically heated with a cut-off arrangement to prevent the temperature rising above 60° C.

Glue for Joinery Work.

It may be of interest to sketch some of the common applications of glue. Joinery work may be done by machine or by hand. A glue of low to medium grade is used (7-8 C.P.) at a glue : water ratio, between 1 : 1½ and 1 : 3 and a temperature of 40-60° C. It is essential to have a viscosity suited to the wood and this can be arranged by altering the grade, the water ratio or the temperature. Porous woods for example need a more viscous glue liquor than hard woods. The glue liquor must penetrate sufficiently into the wood to fill up the first layer of pores—it will not do this if it is too thick—on the other hand, if it is too thin, it will soak right into the wood and leave no adhesive layer on the surface. Machine joinery is particularly exacting because the time during which the joint is under pressure is restricted. It is, therefore, particularly important that each delivery of glue is absolutely uniform, so that the glueing machine once set will continue to function correctly.

Glue for Veneering Work.

Veneering work also calls for a low to medium viscosity glue—there is the additional necessity that the glue must be tacky, i.e., able to hold the veneer in position while it is being transferred to the press.

Glue for Carton Work.

Carton work also demands a tacky glue—generally a low viscosity with about equal weight of water. When porous card is used then a glue of higher viscosity is indicated.

Glues for Other Trades.

The sandpaper and emery wheel trade take a much higher grade (viscosity 9-12 C.P.), because strength of the adhesion is very important.

The paper trade takes medium to high viscosity glues for coating and tub sizing.

The match trade calls for a glue of medium viscosity and, of course, it must be compatible with the other ingredients of the match composition.

The distemper trade is very exacting in its choice of glue, because slight variations will affect the brushing properties of the product. Questions of keeping quality and compatibility with pigments are also of major importance.

CHOCOLATE MANUFACTURE AND CONTROL

PART I.--THE MANUFACTURING PROCESS

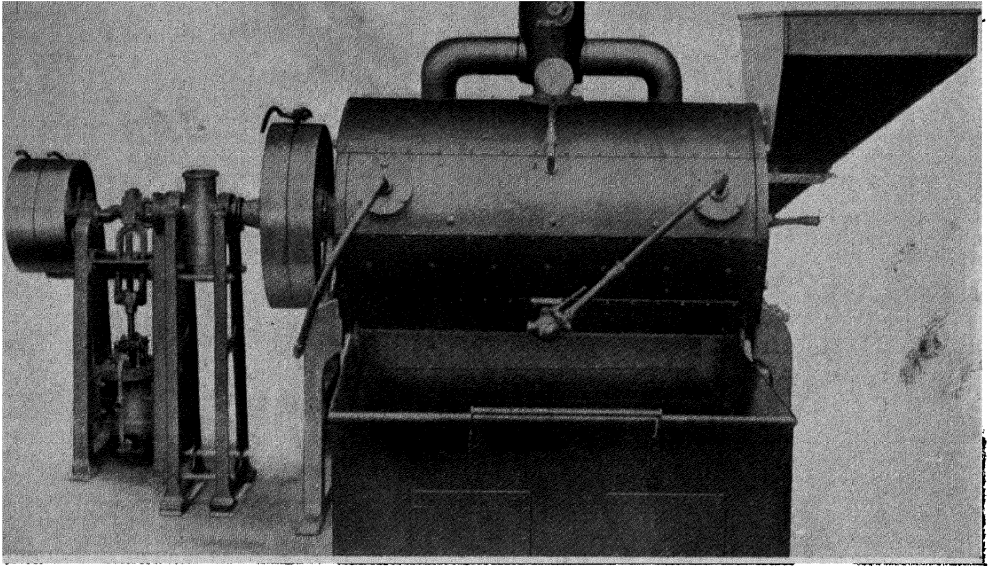


FIG. 1.—STAGES IN CHOCOLATE MANUFACTURE

The first stage after brushing and cleaning consists of roasting the beans in a rotating cylindrical vessel the outer surface of which is heated by gas burners

THE main ingredients of chocolate are cacao beans, sugar and cocoa butter or other fats

Sugar has already been dealt with elsewhere so that we have only to deal briefly with cacao beans and cocoa butter before passing on to describe the various stages in the manufacture of chocolate.

Cacao Beans.

Cacao beans are the seeds of a tree (*Theobroma Cacao*) which grows in tropical regions. The fruit of this tree is an ovoid pod some 7 to 10 inches in length and 3 to 4 inches in diameter. The interior of the pod consists of five cells each of which contains a number of seeds embedded in a soft pinkish pulp; at this stage the beans are pale in colour and practically tasteless. When the pods are ripe they are cut down from the tree, split open with a chopper

and the pulp and beans scooped out. The contents of the pod are then transferred to large wooden boxes in which they are allowed to ferment for a period.

The Fermentation Process.

This fermentation process removes the adherent pulp, kills the germ of the seed and brings about a series of complex chemical changes in the bean, it is a very important process and the aroma and flavour of the final chocolate is to a large extent dependent on the initial care taken during the fermentation. The most notable change is in colour and flavour, the seeds develop their brown colour and the aroma and flavour characteristic of chocolate.

After fermentation the beans are dried or cured by exposure to the sun and are then ready to be bagged and exported to the chocolate manufacturers.

Cacao beans originated from South America, but are now also grown in West Africa, West Indies and Ceylon. Each variety has different characteristics but the average composition as received in this country is :—

	Per cent.
Dry nib	80-83
Water	6-7
Shell and germ	11-13
Number of beans to 1 oz. ..	20-24

The nib, which is, of course, the essential part of the cacao bean, contains 50-55 per cent. of fat (cocoa butter) and 5-6 per cent. of water, whilst the remainder of the cacao matter consists of a complex mixture of albuminoids and other nitrogenous bodies, cellulose, starch, alkaloids (theobromine and caffeine), organic acids, cacao red and mineral salts.

Cocoa Butter.

Except in chocolate containing an unusually high proportion of cacao beans, the amount of cocoa butter introduced by the weight of beans used is not sufficient to render the chocolate workable during the various stages of its manufacture and use. Hence, it is necessary to add at various stages in the manufacture additional amounts of cocoa butter to obtain a smooth flowing chocolate.

Cocoa butter is produced as a secondary product in the manufacture of cocoa powder for drinking purposes. The beans are roasted, winnowed and ground in a manner described in this article and are then subjected to pressure in a warm hydraulic press. The molten fat flows through the pads of the press and is blocked off in tins. It can then be used for chocolate manufacture in the same factory, or in the case of large producers of cocoa powder, where an excess is obtained, it is

sold to other chocolate manufacturers or to the pharmaceutical and other industries.

In addition to the cocoa butter obtained by hydraulic pressure of the nibs a certain amount is extracted by solvents from the cocoa shell which contains about 3.5 per cent. of fat. Cocoa butter obtained in this manner is inferior in flavour to the normal product.

In the cheaper grades of chocolate it is not always an economic proposition to use cocoa butter as the additional fat, and in such cases cheaper fats such as Borneo tallow (which closely resembles cocoa butter), palm kernel and coconut

stearines are used. In milk chocolate the natural butter of the dairy products used serves as part of the additional fat, but this is offset by the fact that milk chocolate contains a lower percentage of cocoa nib than the ordinary plain chocolate.

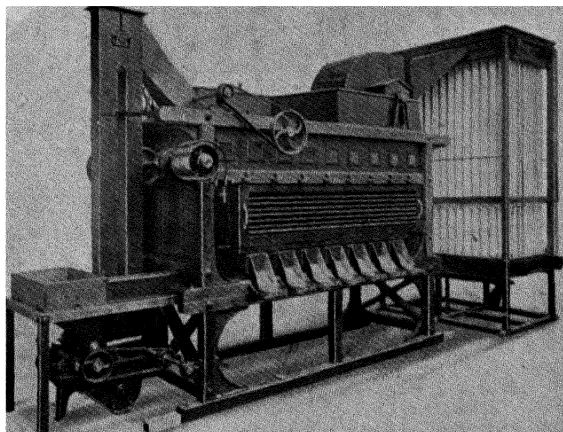


Fig. 2. STAGES IN CHOCOLATE MANUFACTURE.

The next process is to remove the shell which has been rendered brittle by roasting; this is done by passing the beans through a winnower.

STAGES IN CHOCOLATE MANUFACTURE.

Roasting.

After a preliminary brushing and cleaning the beans are ready for roasting, which not only renders the shell easy to remove but also develops the flavour of the bean and drives off part of the remaining acidic substances formed during the fermentation process.

The roasting is performed in a rotating cylindrical vessel the outer surface of which is heated by gas burners or in a globular shaped vessel so constructed that a current of hot air (which has passed through a gas burner) is blown through the rotated beans.

Winnowing.

The next process is to remove the shell which has been rendered brittle by the

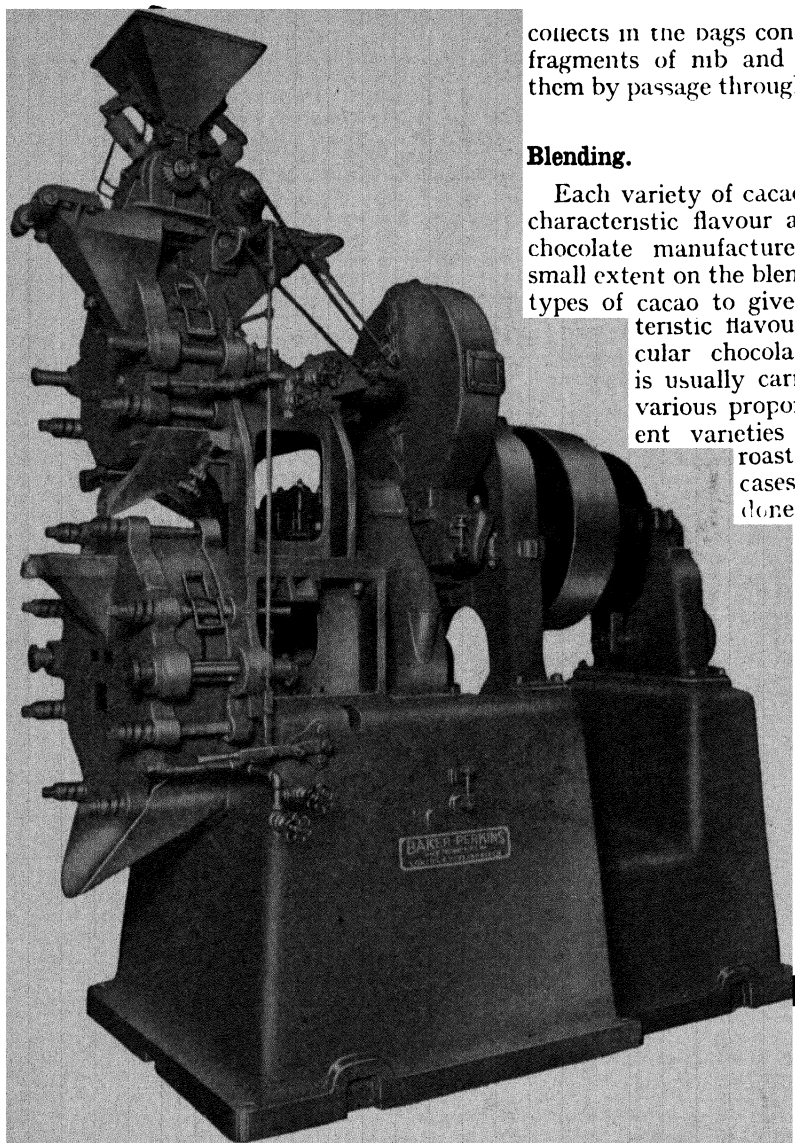


Fig. 3—STAGES IN CHOCOLATE MANUFACTURE

After sorting and blending the nibs are passed through a mill before being incorporated with other ingredients of chocolate.

roasting; this is done by passing the beans through a winnow. The beans are first cracked by passing through adjustable rollers, which ensure the nib is not crushed, and then pass on to rotating cylindrical sieves which separate the nib into various sizes whilst the lighter shell is removed by an air draught. The germ of the cacao bean, which is harder and more fibrous than the rest of the nib,

collects in the bags containing the smaller fragments of nib and is separated from them by passage through a special machine.

Blending.

Each variety of cacao bean has its own characteristic flavour and the art of the chocolate manufacturer depends to no small extent on the blending of the various types of cacao to give the final characteristic flavour to his own particular chocolate. This blending is usually carried out by mixing various proportions of the different varieties of nibs after the roasting, but in some cases the blending is done prior to roasting.

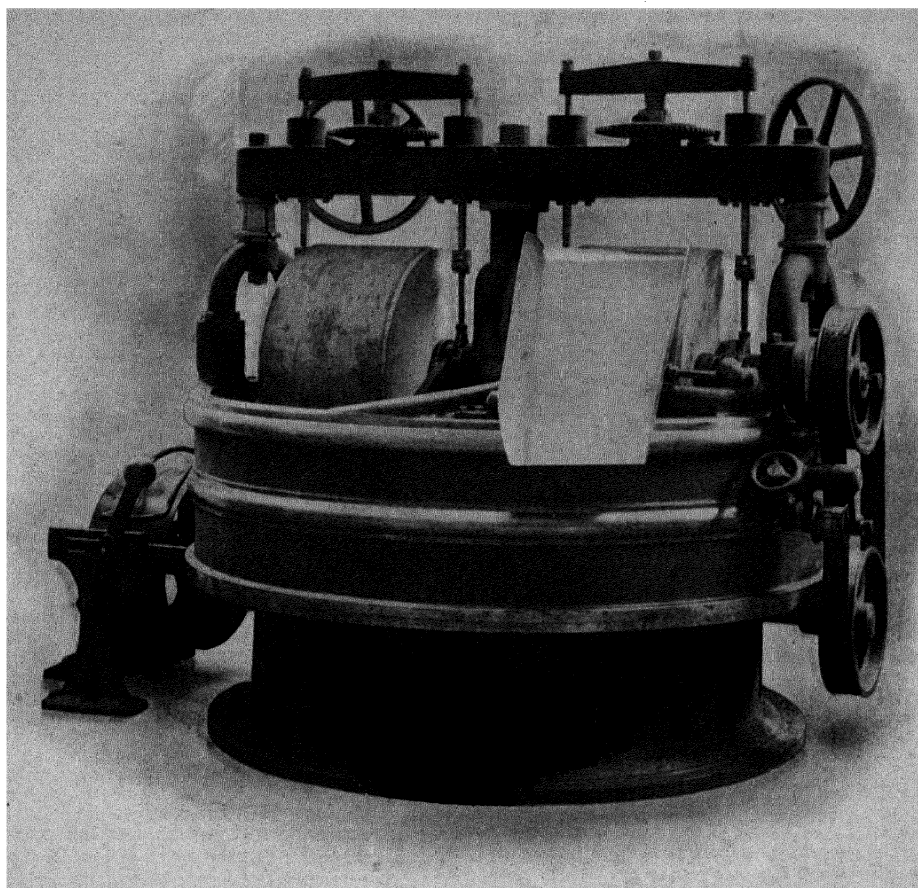
Grinding of Nibs.

Before the blended nibs are incorporated with the other ingredients of chocolate they are ground to a smooth mass by passage through horizontally turning stones the faces of which are grooved to obtain a maximum grinding effect. After passage through a series of these mills the nibs emerge as a liquid mass. This old method is being sup-

planted by a rough grinding through grooved metal rollers, followed by passage through steel rolls and subsequent transference to a steam-heated kettle.

Grinding of the Sugar.

Granulated sugars of the higher grades of refinement are used in chocolate manufacture but a slight yellow tinge in the sugar is immaterial. It is, however,



revolves. Special scrapers are fitted to guide the chocolate mass continually under the rollers.

generally considered essential that the sugar should be ground to a fine powder before it is incorporated with the nibs.

There is a variety of sugar mills on the market for this purpose, and the general principle adopted is to feed the sugar into a closed vessel in which rotating metal pins or beater arms beat the sugar by impact into fine particles.

Mixing.

When the nibs and sugar have been suitably prepared they are mixed in a melangeur which consists essentially of a revolving steam-heated bed-plate of steel or granite, upon which rest two granite rolls which are driven round when the bed-plate revolves. Special scrapers are fitted to guide the chocolate mass continually

under the rolls. These rolls are fitted with lifting gear to enable them to be lifted clear of the bed plate in the earlier stages when the mass is coarse in size or stiff in texture.

The melangeur is first warmed and then the nibs or cocoa mass are introduced and run down to a liquid paste. Part of the sugar is now added and since the sugar particles soak up the free fat, the mass becomes stiffer in texture. The mass is allowed to run for a while in order to restore its fluidity and some of the additional fat is added. By repeating these operations all the sugar is gradually added and the mass reduced to a smooth liquid paste.

Refining.

To obtain the smooth chocolate, which

the present day public demands, it is essential that the particles of cocoa and sugar should be as fine as possible and this is effected by passing the chocolate after mixing in the melangeur through a refiner. The modern refiner consists of a series of vertical water-cooled steel rolls which are geared to rotate at different speeds so that a shearing as well as a crushing action is exercised on the particles.

The chocolate emerges from these refiners in dry flakes since the further diminution in the size of the particles of sugar results in a further soaking up of the fat. The amount of additional fat added in the melangeur is so adjusted that this maximum grinding effect is obtained on the refiner. If too much cocoa butter is added the crude chocolate is too thin to give a good film on the rolls of the refiner, and conversely if too little butter is added, the chocolate is too "pasty" for feeding through the rollers.

Stoving.

After refining it is still the practice of high-class manufacturers to stove the chocolate for a period (1 to 3 days) in a hot room at about 140° F. This practice is said to improve the flavour and consistency of the chocolate.

Conching.

This final stage in the manufacture is an extremely important one. It consists of a continual agitation of the chocolate in a machine designed to ensure com-

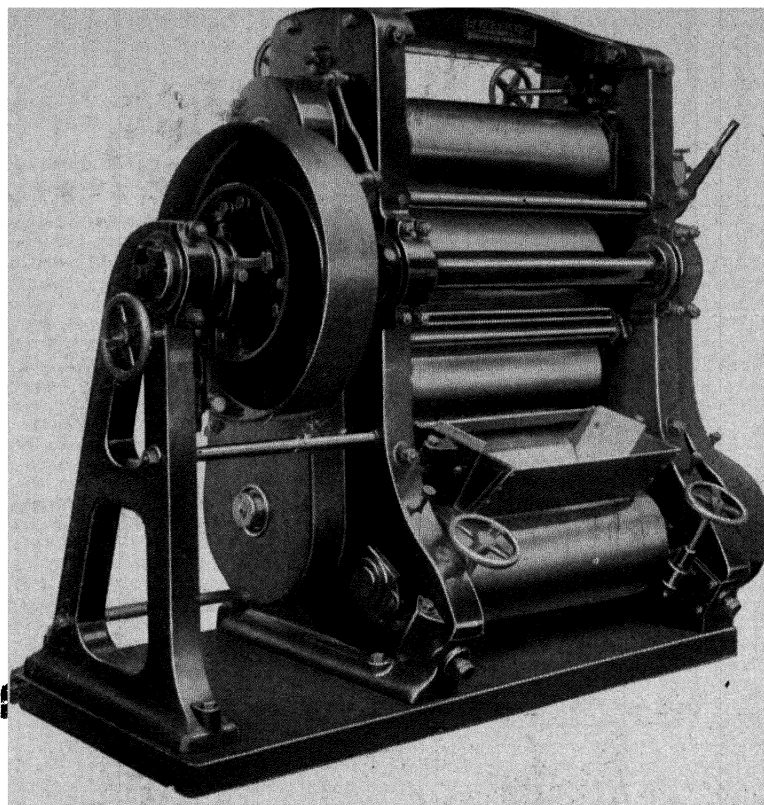


Fig 5 —STAGES IN CHOCOLATE MANUFACTURE.

The particles of cocoa and sugar are next passed through a refiner to make them as smooth as possible.

plete homogeneous mixing of the various ingredients so that each particle of sugar is coated with cocoa butter. At the same time the process has definite beneficial effects on the development of flavour in the finished chocolate. Thus the final traces of the volatile acids and other volatile organic substances produced in the earlier treatment of the beans are removed and the chocolate loses any harshness of flavour and develops a smooth, velvety taste to the palate.

The conche consists of two pairs of pots with curved end-plates in which steel or granite rolls, actuated by a plunger arm, travel to and fro pushing a wave of chocolate before them. They are heated by gas or steam and the temperature of the chocolate and the period for which it is conched varies amongst various manufacturers.

At the beginning of the conching stage the final portions of additional fat are usually added and also any essences or flavouring matters.

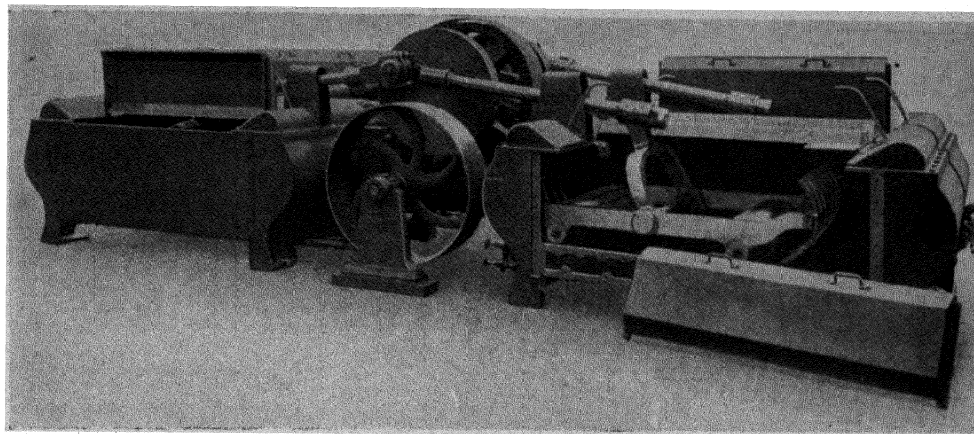


Fig. 6.—THE FINAL STAGE IN CHOCOLATE MANUFACTURE.
This consists of a continual agitation of the chocolate in a machine known as a conche.

Storage.

On leaving the conche the chocolate is ready for use and can be run into tins or blocked off for future occasions, or, if required for immediate use, stored in storage kettles, which are water-jacketed steam or gas-heated vessels fitted with a stirring device.

Such stirring devices are so devised that they rotate in a horizontal as well as a vertical plane to ensure no

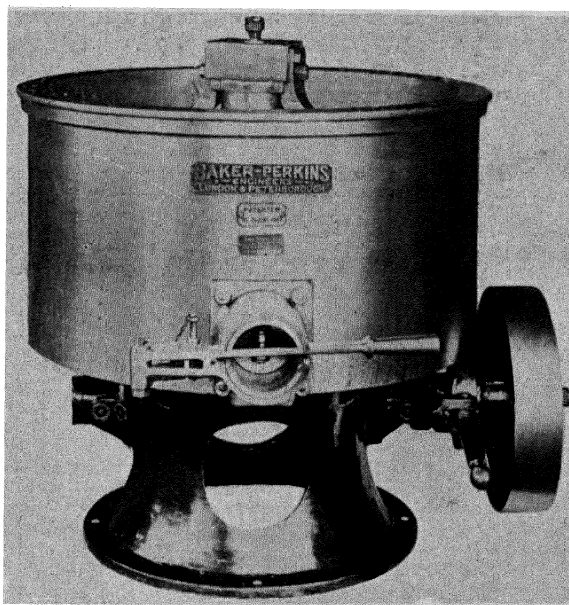


Fig. 7.—A CHOCOLATE STORAGE KETTLE.

analytical control of chocolate manufacture, separation out of the molten fat. In this form the chocolate may be drawn off to be moulded into bars and other more fanciful shapes, or for use as couverture on various types of centres.

We are indebted to Messrs. Baker, Perkins, Ltd., for permission to reproduce the illustrations which accompany this article.

A later article deals with the

THE MANUFACTURE OF PICKLES AND SAUCES

PART II.—ROUTINE CHEMICAL TESTS

ROUTINE chemical tests are necessary at every stage in the manufacture. It is necessary in the first stage to know the salt content of the vegetables in order to be sure that the brining has been sufficient. This is done by estimating the salt as chlorides.

Determining the Salt Content.

Five gms. of the material is boiled with 75 ml. to 100 ml. of water in a beaker for a few minutes in order to extract the salt. The watery extract is decanted along a glass rod through a funnel and into a 250-ml. flask. More water is added to the solid, which is boiled again. The second extract is then added to the first in the 250-ml. flask and the process repeated once more. The solution is cooled and made up to the 250-ml. mark with cold distilled water. 50 ml. is pipetted into a conical flask and a few drops of a 10 per cent. solution of potassium chromate added. Silver nitrate solution (N/10 silver nitrate 16.99 gms. per litre) is then run in carefully from a burette until the yellow colour of the solution changes to red. The number of ml. of the N/10 silver nitrate needed for the titration multiplied by .00585 gives the weight of chlorides expressed as sodium chloride in the

sample taken, from which a simple calculation gives the percentage.

Brine in Pickled Olives.

An exactly similar test is necessary for the finished pickled olives. When carrying out this test it must be remembered that a satisfactory end point of the colour change is only possible in a neutral solution. In the case of vegetables from brine, no neutralisation is necessary, but when dealing with an acid solution, alkali must be added until the sample is neutral to litmus.

In the event of the solution being alkaline, nitric or acetic acid is used for neutralising. If, as sometimes happens, organic matter from the vegetables interferes and prevents there being a satisfactory

end point, the weighed vegetable is thoroughly mixed with lime (which must, of course, be free from chlorides) and then carefully charred over the flame of an Argand burner; the char is extracted with hot water and the extract neutralised and titrated as usual.

No tests are necessary after the debrining or weak acidic stage unless the vegetable is to have no further treatment; that is, if it is to be pickled straight away in 5 per cent. vinegar and bottled.

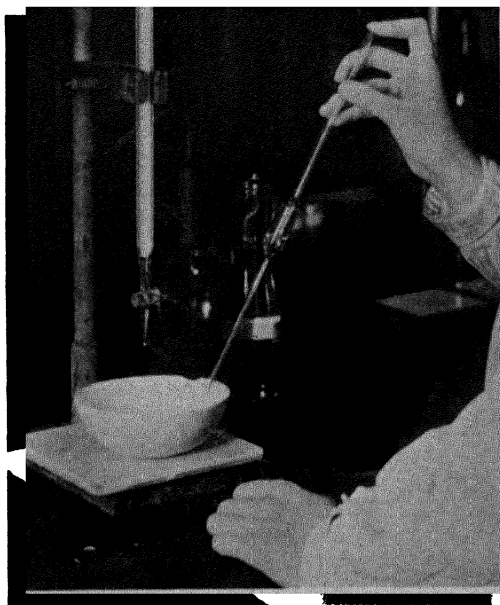


Fig. 1.—DETERMINING THE STRENGTH OF THE BRINE (1)

After the appropriate dilution a measured quantity is titrated with standard silver nitrate solution

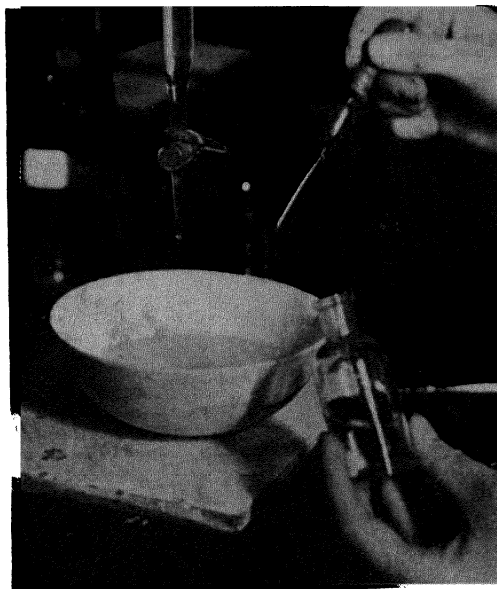


Fig. 2.—DETERMINING THE STRENGTH OF THE BRINE (2).

A few drops of potassium chromate solution are added to the salt solution as an indicator, and the silver nitrate solution is run in with constant stirring.

Strength of Vinegar.

If there are any doubts about the strength of this vinegar (usually between 5.2 per cent. and 5.5 per cent. as acetic acid) 10 ml. can be titrated with $N/2$ soda, the soda being allowed to run in slowly from a burette into the flask containing the 10 ml. vinegar to which a few drops of a 1 per cent. solution of phenolphthalein have been added to act as an indicator. When the colour has changed to very pale pink the number of ml. required is noted and multiplied by 0.3, which gives the acid strength as grammes of acetic acid per 100 ml.

TEST FOR ACETIC ACID CONTENT.

All pickles and sauces have to be tested for acetic strength. With sauces the same procedure is adopted as for vinegar except that, of course, the material is weighed out in the first place and is not pipetted. With pickles, however, the case is different, for the acid has to diffuse slowly through the cell walls of the vegetables and a technique of shaking and leaving is adopted. The weighed material is washed into a wide mouthed stoppered jar of about 400 ml. capacity. Distilled

water is added until the jar is about half-filled and the indicator is then put in. The half normal solution of soda is then run in from a burette until the colour change has taken place. The jar is then stoppered and shaken vigorously; the colour disappears immediately. Further soda is added until the colour seems permanent. The jar is allowed to stand for half an hour and after that period more soda is run in until the red colour change takes place. It is then stoppered and shaken again for a minute or two, allowed to stand for a further 20 minutes, and the titration finished by shaking the jar after the addition of every few drops of soda.

The number of ml. of soda used after each period of titration should be noted down for routine purposes on a gummed label on the jar stuck on for that purpose. The sum of these can then be calculated to acetic acid in the usual manner.

SUGAR ESTIMATION.

Once a sweet pickle or sauce has been made up and found to be satisfactory,

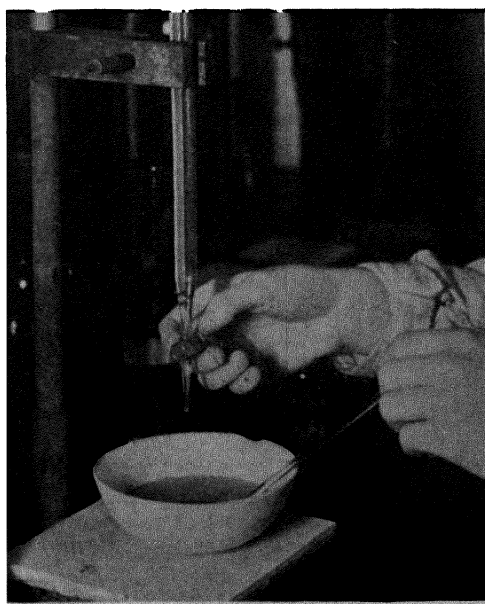


Fig. 3.—DETERMINING THE STRENGTH OF THE BRINE (3).

When the titration is completed, the colour of the solution changes from yellow to pink, on account of the formation of red silver chromate by the first drop of silver nitrate solution in excess of that required to react with the salt present. The white porcelain dish holding the solution makes the colour change readily obvious.



Fig 4—TESTING PICKLES FOR ACIDITY

A weighed quantity is washed into a wide-mouthed stoppered bottle, water is added followed by 1 ml phenolphthalein solution and then standard sodium hydroxide solution from a burette, with vigorous shaking between successive additions, until a permanent pink tint is obtained.

it is necessary that it shall become standardised and shall not vary in its sugar and acetic content.

In finding the sugar content of sweet pickle it is usual to estimate it as sucrose. The methods of sugar estimations have already been described in detail elsewhere, but the following method is rapid, and gives results of sufficient accuracy for routine purposes. A convenient quantity of material to be tested is weighed out, washed into a beaker, boiled and extracted as is done in the salt determination test.

The watery extracts containing the sugar are decanted or strained (the latter in the case of sauces) into a flask of convenient capacity. It is now cooled and made up to the capacity mark with cold distilled water. The repeated boiling has now in all probability inverted all the sugar, but in order to make quite certain that the inversion of the sugar is complete, a flask graduated at 100 and 110 ml. is filled to the

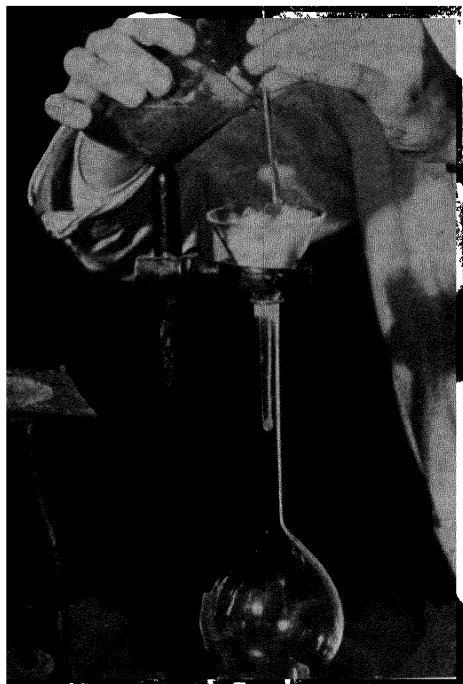


Fig 5—DETERMINATION OF SUGAR IN A SWEET PICKLE.

A weighed quantity of the pickle is boiled with distilled water, which is then decanted through a cotton filter into a graduated flask, and the process completed as described in the text.

100 ml. mark with the extract and placed in a water bath at 68° C.

After five minutes, concentrated hydrochloric acid is added until the liquid very nearly reaches the 110-ml. mark. After 10 minutes, during which time the temperature of bath must be constant at 68° C., the flask is taken from bath and rapidly cooled. The contents are washed through a funnel into a 200-ml. flask, neutralised with strong sodium hydroxide (about 30 per cent. NaOH) solution (using methyl orange as indicator, the colour change being from red to orange), and then filled up to the 200 ml. graduation mark with distilled water.

The Fehling's Solution.

Some of the solution is now poured into a burette and allowed to run into 20 ml. of boiling mixed Fehling's solution, about 0.3 ml. at a time, giving a small shaking after each addition. The Fehling must

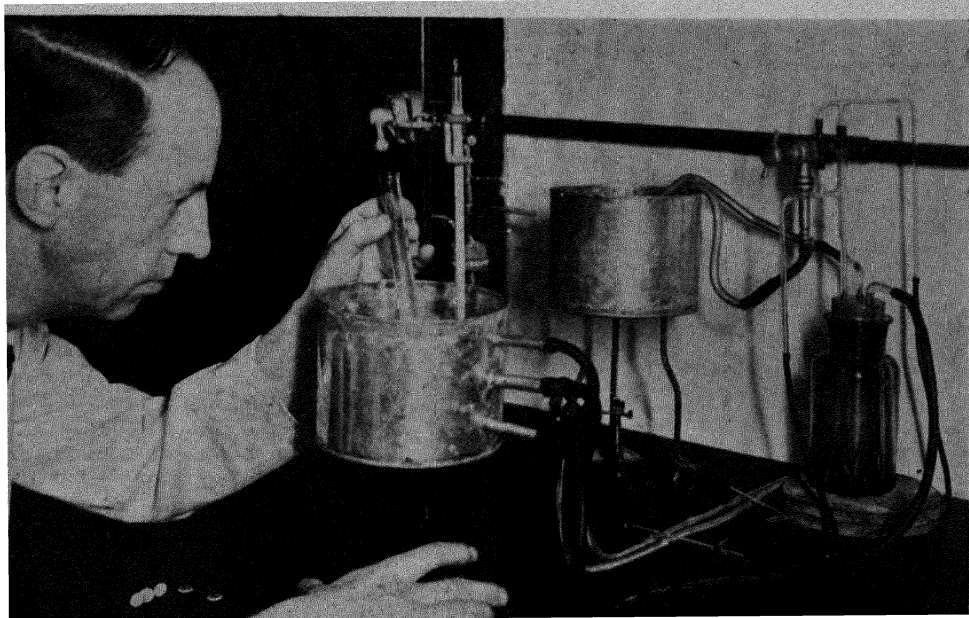


Fig. 6.—To MAKE SURE THAT ALL THE SUGAR IS COMPLETELY INVERTED, THE SOLUTION IS HEATED AT 68° C. WITH HYDROCHLORIC ACID.

The photograph shows a water bath in which this is being done. The water flowing through the bath is maintained at the correct temperature by means of the thermostatic control on the right of the picture. This consists of an arrangement by which the supply of gas which heats the water is automatically increased or diminished as the temperature falls or rises.

boil fairly rapidly all the time the titration proceeds. The blue colour of the Fehling's fades and red cuprous oxide is precipitated. When the blue colour has nearly disappeared, 5 drops of a 1 per cent. aqueous solution of methylene blue is added. At this juncture the extract in the burette is added drop by drop, with a pause of 15 seconds and a slight shaking between each until at length a brick red colour is reached when all the copper in the solution is reduced. The titration should be

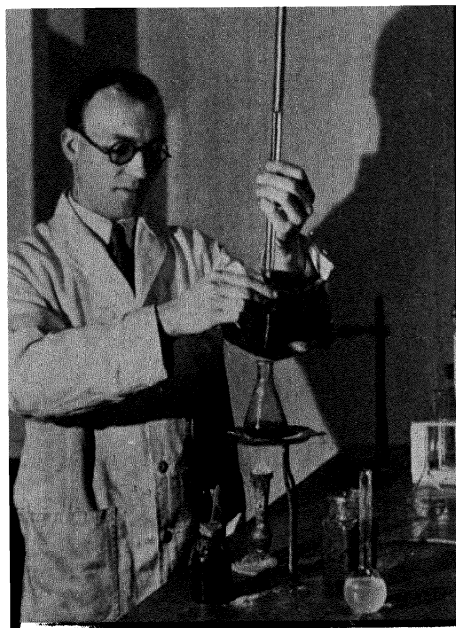


Fig. 7.—THE INVERTED SOLUTION IS NEUTRALISED AND RUN INTO A MEASURED QUANTITY OF FEHLING'S SOLUTION CONTAINED IN THE FLASK.

between 15 and 25 ml.

How to Calculate Proportion of Sugar.

To calculate the proportion of sugar with sufficient accuracy for routine purposes, it may be assumed that under the conditions of the test, the volume of sugar solution necessary to reduce 20 ml. of the mixed Fehling's solution is inversely proportional to the concentration of the sugar solution. Since 20 ml. of a 0.5 per cent. solution of invert sugar is required to reduce 20 ml. of the

mixed Fehling's solution, a simple method of calculating the percentage of sugar in the material being tested, is as follows —

Calculate by simple proportion how many ml. of a 0.5 per cent. extract of the material would reduce 20 ml. of the mixed Fehling's solution, divide 20 by this figure, and multiply the result by 100. For example, suppose 10 gms. of a sweet pickle is extracted with hot water as described, and after inversion and neutralisation the combined extracts are made up to 500 ml. This represents a 2 per cent. extract. Next suppose that, say, 17.3 ml. of this extract is required to reduce 20 ml. of the Fehling solution. Then 69.2 ml. of a 0.5 per cent. extract (that is, 17.3×4) would be required on a proportional basis, and the percentage of sugar in the pickle (calculated as in vert sugar) is

$$\frac{20}{69.2} \times 100 = 28.9$$

per cent. If the result is required in terms of sucrose, the figure 19 is substituted for the "20" in the above calculation.

The Fehling's solution is made up by mixing a solution of copper sulphate containing 69.28 gms. of the crystallised salt per litre with an equal volume of an alkaline tartrate solution prepared by dissolving 350 gms. of Rochelle salt and 100 gms. of sodium hydroxide in water and making up to 1 litre. Before titration, it is usual to add to the 20 ml. of mixed Fehling's solution an equal volume of distilled water; also a pinch of powdered pumice or broken porcelain in the 150 ml. conical boiling flask will prevent bumping.

VISCOSITY TEST.

The other test that is of importance is

that of viscosity. For rather rough and ready work a standard can be set by noting the time taken by a sauce in getting through a funnel with an orifice of a size that must be rigidly kept for all further testing. However, this method is rather crude. Duplicate samples rarely give close agreements so that an instrument has been designed whose utility does not rest upon time taken by test materials to pass

through an orifice, but on the slowing down of a metal cylinder suspended by a wire that has been twisted against its natural point and is springing past its original position. This is the torsion viscometer, and by its use comparative results are obtained which can be duplicated. This instrument is simple in operation and easy to use.

Using the Torsion Viscometer.

A beaker containing the sample to be tested is placed on the movable table underneath the suspended cylinder, and the viscometer operated in the usual manner.

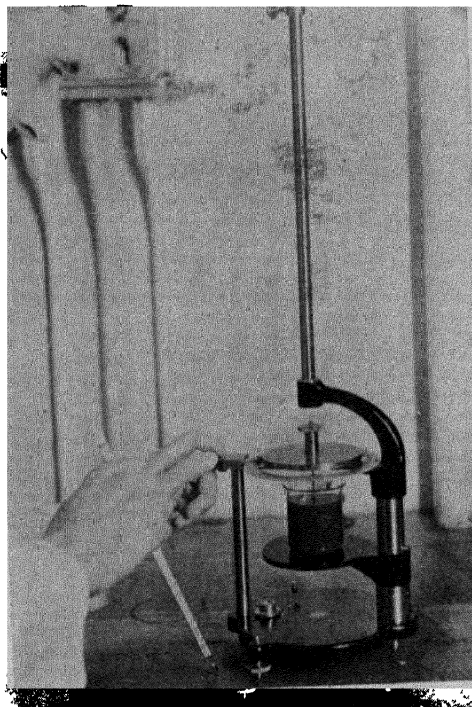


Fig 8 — TESTING THE VISCOSITY OF A THICK SAUCE BY MEANS OF THE TORSION VISCOMETER
As the viscosity changes with the temperature of the liquid, this must be known.

Controlling the Manufacturing Process.

For controlling the manufacturing process the usual method of use is to take a standard sample of the required viscosity and determine the reading obtained. This is repeated at several different temperatures over the range likely to be required in the pickles department. A graph is then plotted showing the required deflection against temperature. Samples from every batch made are tested out in this way and kept up to standard, so that if the standard set in the first place is scientifically sound, no separation of liquid and solid constituents will take place.

PAINTS AND VARNISHES

PART IV.—TESTS ON PAINT

By H. COURTNEY BRYSON

The Mobilometer.

It is sometimes desired to measure the mobility of a paint and attempt to correlate this with brushing properties, and a special instrument—the mobilometer—has been designed for this purpose.

The room temperature must be kept constant for all readings. The cylinder (Fig. 1) is filled with material to the mark. The plunger is inserted and forced to the bottom. A mark is made upon the rod at the top of the bracket when the plunger is at the bottom of the cylinder.

Another mark is made 20 cm. below the first mark. The plunger is then raised so that the second line coincides with the top of the bracket, care being taken to make sure that the disc at the end of the plunger is covered with paint. A weight is applied to the pan on top of the plunger and the time in seconds for the first line on the rod to coincide with the bracket determined with a stop watch.

Repeat the Procedure with Different Weights.

If desired, the procedure may be repeated with a number of different weights and the points plotted on a curve. Decidedly plastic materials like heavily pigmented flat wall paints give curves when the results are plotted out, while viscous

materials like fine enamels give straight lines.

Interpretation of the Results.

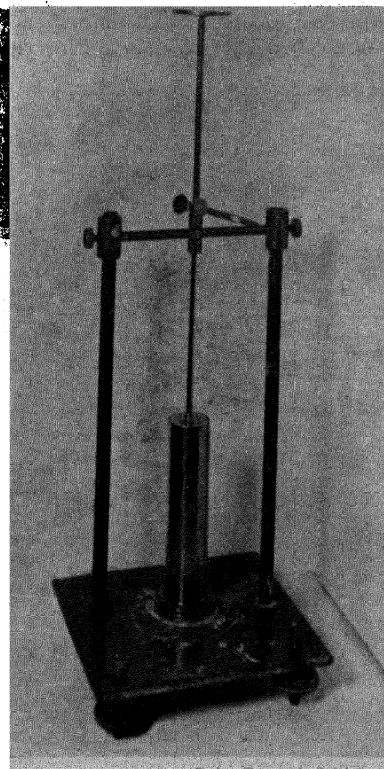
The chief difficulty lies in the interpretation of the results, since the mobilometer measures an only partly known mixture of properties. Differences in the degree of wetting of the pigment lead to differences in mobility. In this connection, too, it should be noted that moisture, for instance, exerts an enormous influence on the plasticity of a paint, 0.5 per cent. raising the yield value of a particular paint from 90 to 3,450, simultaneously reducing the mobility to one-fourth its former value. Long grinding generally reduces the mobility, probably due to oxidation of the medium. There is a relationship between mobility and viscosity.

The Measurement of Hiding Power.

The hiding power of a paint (which has nothing to do with its covering power or spreading capacity) is that thickness of paint which is necessary just to obliterate completely any background upon which it may be spread. Since obliteration is often the major function of a paint, the determination of the weight or volume required to hide a given area is obviously of prime importance.

The Simplest Method.

The simplest method

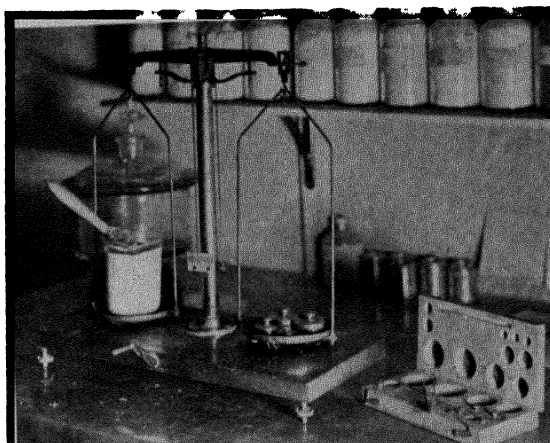


Paint Research Station.
Fig. 1.—THE MOBILOMETER.
For measuring the mobility of paint.

is to paint a piece of linoleum containing black and white squares (Fig. 3). The lino is first rubbed with oil to fill the pores and then wiped clean. The can, with the paint and the brush, is then weighed and a dab of the paint placed on each black square and then thoroughly brushed out in the usual manner.

If complete obliteration is not achieved more paint is applied till the brightness contrast over the whole area is reduced to zero.

The can and brush are then reweighed and the result expressed as the number of square yards hidden per gallon of paint. The lino can be cleaned and used a number of times. It should be noted that



Brent Manufacturing Co., Ltd

Fig. 2—THE SIMPLEST METHOD OF MEASURING HIDING POWER (1)

A beaker full of paint and the brush are weighed.

the hiding power of paint films may either increase or decrease as drying proceeds. For instance, a casein water paint containing chalk as a pigment is very transparent while wet, but increases enormously in opacity when dry.

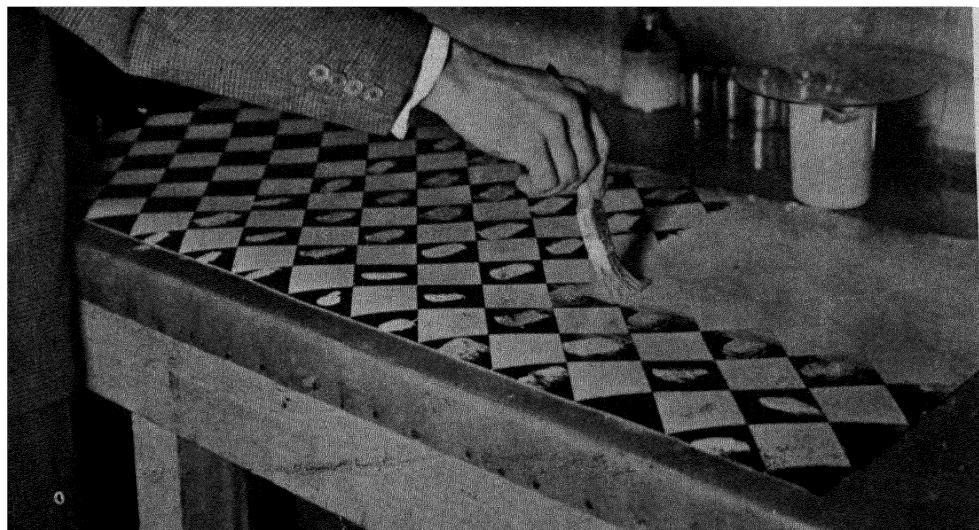
The Pfund Cryptometer.

Contrast obliteration may be measured

more accurately by means of the Pfund cryptometer, which is probably the most widely used instrument for this purpose, though subject to the limitation that a background is always involved.

The Transmeter Method.

The Transmeter developed by the Paint



Brent Manufacturing Co., Ltd

Fig. 3—THE SIMPLEST METHOD OF MEASURING HIDING POWER (2).

A given area of linoleum previously filled with linseed oil to stop absorption is then painted over with the paint. The method of securing even distribution is shown. If complete obliteration is not obtained in one coat a second is applied and so on until complete hiding is obtained, the beaker being kept carefully covered meanwhile. Finally the beaker and brush are reweighed and the result expressed as the hiding power in sq ft /gallon.

Research Station is a sensitive instrument and can be used to measure the hiding power of white or coloured pigmented films in either the wet or the dry condition. The principle of the instrument depends on the relationship which exists

between the hiding power of the paint film and its property of transmitting light. In other words, a film sufficiently thick to obliterate the contrasting areas of a given background transmits diffused light of a standard intensity independent of the nature of the film.

The Apparatus.

The apparatus is illustrated

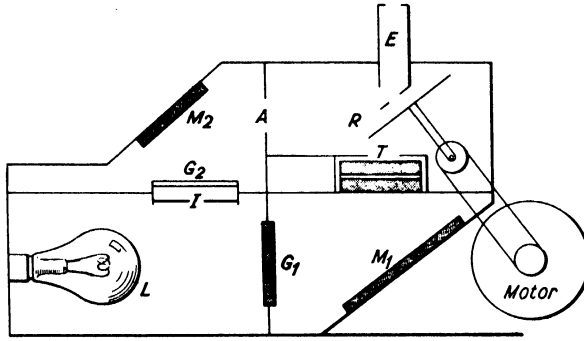


Fig. 4.—DIAGRAMMATIC VIEW OF TRANSMETER USED FOR MEASURING HIDING POWER.

A, aperture; E, eyepiece; G₁ and G₂, diffusing screens; I, iris diaphragm; L, lamp; M₁ and M₂, mirrors; R, rotating sector; T, paint wedge.

in Fig. 4. Two beams of light travelling in different directions from the lamp are isolated by suitable diaphragms. Light travelling horizontally from the 60-watt lamp L passes through a ground glass diffusing screen G₁, is reflected vertically by the

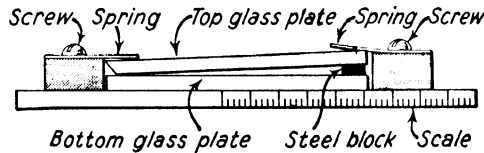
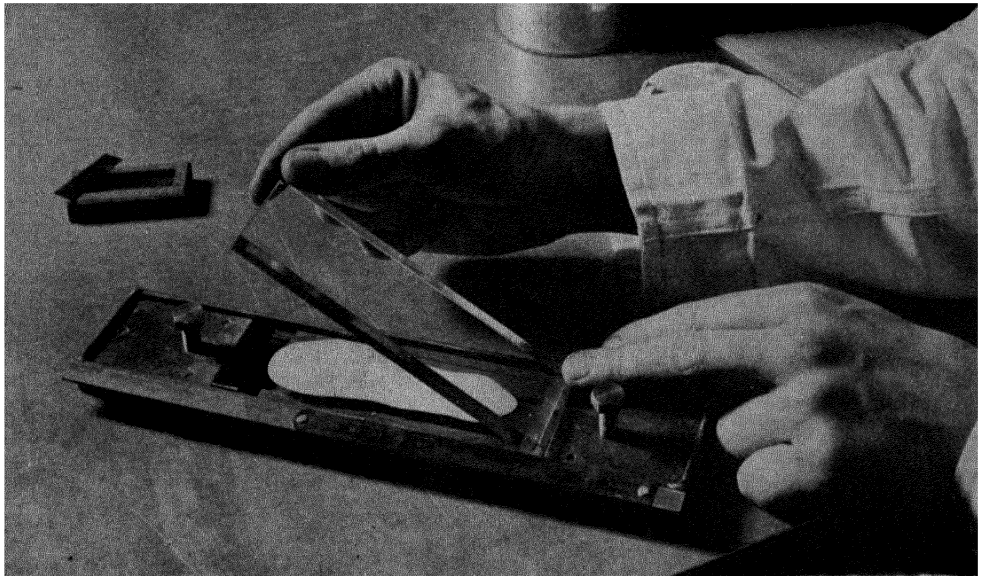


Fig. 5.—DIAGRAM SHOWING CONSTRUCTION OF GLASS PLATES TO GIVE A WEDGE-SHAPED FILM.

mirror M₁ and is then seen through the eyepiece E. Light travelling vertically from the lamp passes through the iris diaphragm I and the ground glass diffusing screen G₂, then is reflected horizontally by the mirror M₂ through an aperture A on to the upper white surface of a rotating sector R, which diffusely reflects the light through an eyepiece E. When the sector is rotating,



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Fig. 6.—MEASUREMENT OF HIDING POWER WITH THE TRANSMETER.

Flowing the paint on the lower glass plate and lowering the top one to obtain wedge-shaped film.

light from the lamp is seen alternately via M_1 and M_2 .

By adjusting the intensity of the two beams of light to equality the flickering produced by the rotating sector may be made to disappear. To cause the flickering completely to disappear, it is necessary to adjust the motor D, which drives the sector, to some definite speed which depends on the intensity of the light, and for this purpose a variable resistance is connected in series with the motor.

How the Paint is Tested.

The paint to be tested is introduced at T in the form of a wedge between two pieces of plate glass separated at one end by a strip of steel of accurately known thickness. The glass plates, which are $\frac{1}{4}$ -in. thick, are carried in a metal tray (Fig. 6) provided with a scale along one side. By moving the tray different points along the wedge-shaped film of paint may be brought vertically under the eye-tube.

The angle of the wedge of paint can be varied by using strips of different thickness, and thus a wide range of hiding powers may be measured. The glass plates are secured in the tray by means of the screws bearing on stout springs.

By this arrangement high pressures which are reproducible can be applied to the ends of the plates at points where no strain can occur in the glass.

A Typical Example.

Suppose a paint film which is just thick enough to produce complete hiding is placed at T in the path of the light from M_1 . When the sector rotates, flickering will be seen in the eyepiece unless the aperture of the iris diaphragm is adjusted

so that the intensity of the light from M_2 is equal to that transmitted by the film at T. Now suppose the diaphragm to be fixed at this aperture and the film removed from T. For a given source of light the intensities of diffused light transmitted by different films which are just able to produce complete hiding of the same background are equal.

Hence if a wedge-shaped film is introduced at T and its position adjusted so that no flickering occurs, the thickness of the wedge at that point vertically under the eye-piece is the hiding thickness of the paint forming the wedge, since at this

thickness the intensity of the light transmitted is equal to that transmitted by the film used for the adjustment of the diaphragm. The calibration control of the instrument is calculated by means of a transmission standard—a piece of photographic film of graded density, which ensures absolutely reproducible results.

Measurement of Hiding Power of Wet Paint.

The lower glass plate is placed in the metal tray and a small quantity of paint placed in the

centre. The metal strip (of suitable thickness) is placed at one end of the lower plate and the edge of the top plate, which is bevelled at 45° to make a sharp contact line, is allowed to rest on the other end. The top plate is then lowered slowly, to allow air bubbles to escape, and pressed slightly to cause the paint to flow out. The screws are then tightened and the tray is placed in the Transmeter and the position of no flicker obtained. This gives the distance x along the wedge at which the hiding thickness is situated. The hiding thickness is given by Txt/l , where t is the thickness of steel strip and l the length of wedge. A paint composed of linseed oil 36.9 per cent. and zinc oxide 63.1 per cent. gave

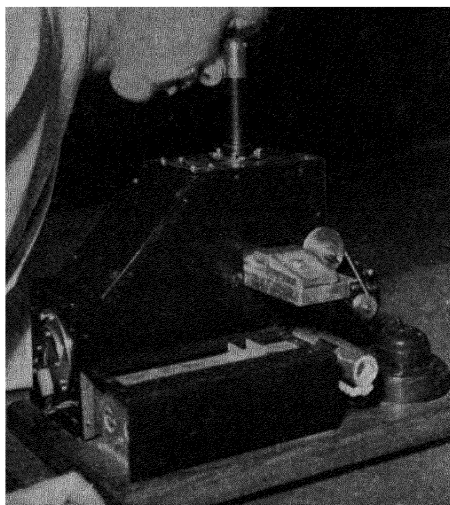


Fig. 7 ADJUSTING THE TRANSMETER TO POSITION OF "NO FLICKER"

Paint Research Station

$x = 7.25$ cm., $t = .04$ cm., $l = 13.5$ cm. From the above formula the hiding thickness is calculated to be .0215 cm., or .00846 in. 1 sq. ft. of the paint at .00846 in. had a volume of $144 \times .00846 = 1.22$ cu. in. Since one gallon = 277.7 cu. in., one gallon of the paint hides $277.7/1.22$ sq. ft. = 228 sq. ft.

Hiding Power of Dry Paint Films.

A graph is drawn connecting hiding thickness ratios with aperture of the iris diaphragm. A wedge or film of liquid paint of known hiding power is placed in the Transmeter at definite positions so that at the points observed on the wedge the film thicknesses are known ratios of the hiding thickness. The corresponding scale readings of the iris diaphragm are obtained when the condition of no flicker is observed. When the wedge film is replaced by the dry film and the iris diaphragm adjusted to give no flicker, the hiding thickness ratio is obtained from the diaphragm scale reading by referring to the graph. The thickness of the dry film can be measured. Owing to the small amount of light transmitted the

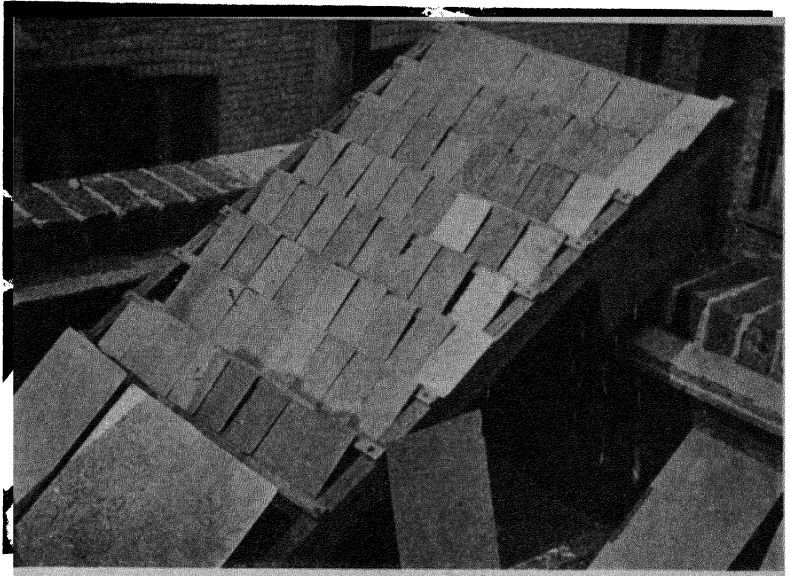


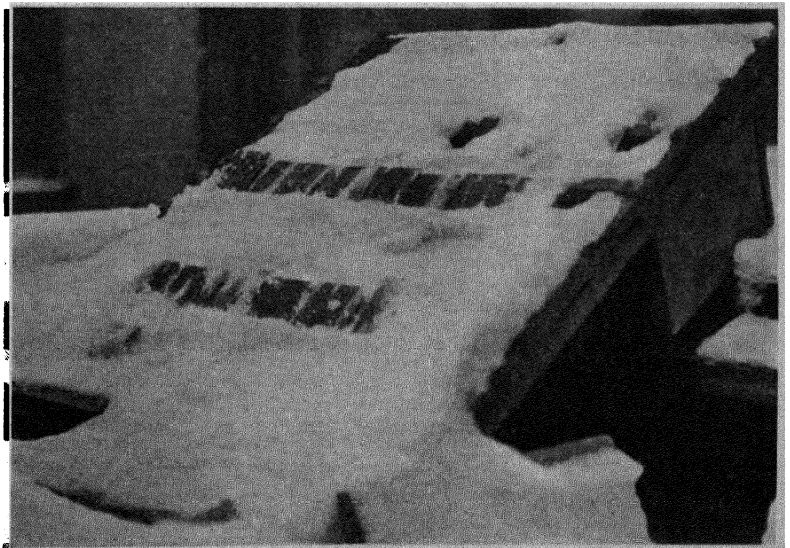
Fig. 8.—WEATHERING TESTS (1).

Panels facing south at an angle of 45 degrees on the roof of a building in the heart of London.

instrument cannot be used for deeply coloured films.

Results Obtained with Transmeter.

Using this instrument it has been shown that the hiding power obtained from a wet film may be 10-15 per cent. higher than



Brent Manufacturing Co., Ltd.

Fig. 9.—WEATHERING TESTS (2).

The panels in Fig. 8 covered with snow. The panels are examined periodically and compared with identical panels exposed in other vicinities, e.g., to sea air.

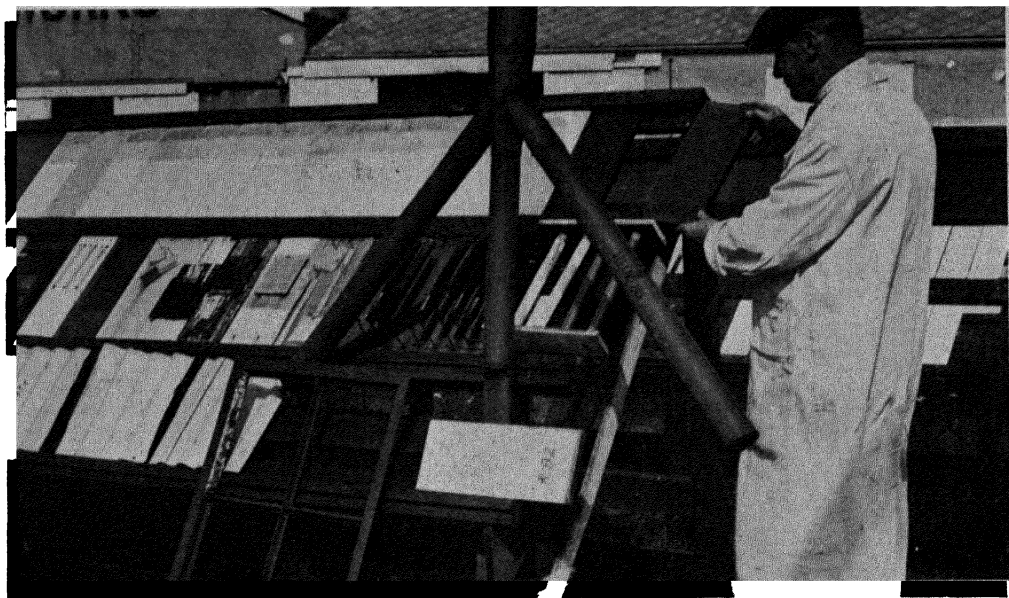


Fig. 10.—PLACING PAINTED PANELS IN AN EXPOSURE RACK *Nobel Chemical Finishes, Ltd*

that obtained when the film is dry and that on account of more pronounced aggregation of pigment particles a greater area may be hidden by unit volume of paint if the material is applied in one thick film instead of two thin ones.

It can also be shown that white paints possess greatly increased hiding power when lightly tinted, e.g., 1 per cent of ilminite black added to titanium white nearly doubles the hiding power of the

paint made from it, while the colour is still lighter than that of white lead.

Where expensive pigments are used the Transmeter enables the exact amount of extender which may be used without impairing the hiding power to be calculated.

Weathering Tests on Paint and Varnish Films.

The usual procedure to determine the durability of a paint is to expose fair-sized

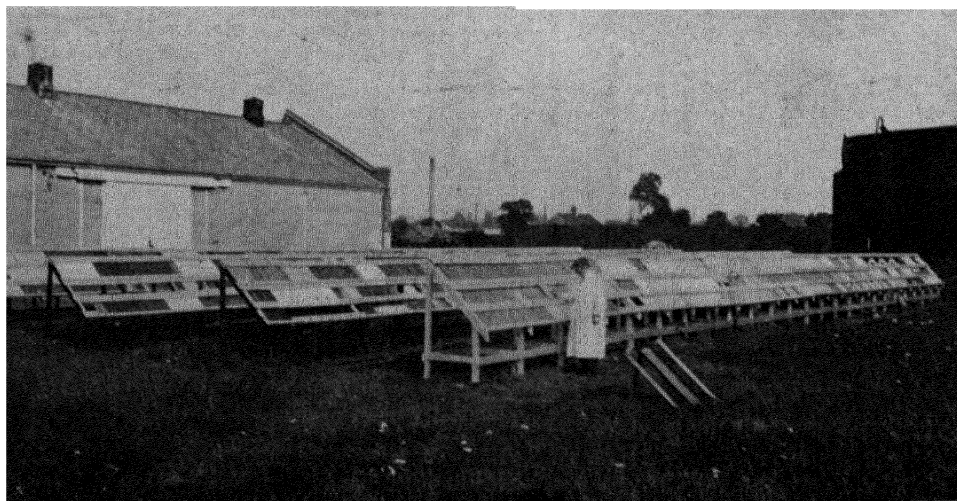


Fig. 11 —THE EXPOSED PANELS ARE EXAMINED PERIODICALLY. *Nobel Chemical Finishes, Ltd*

panels in different districts and on different surfaces to the effects of weather for long periods till breakdown occurs.

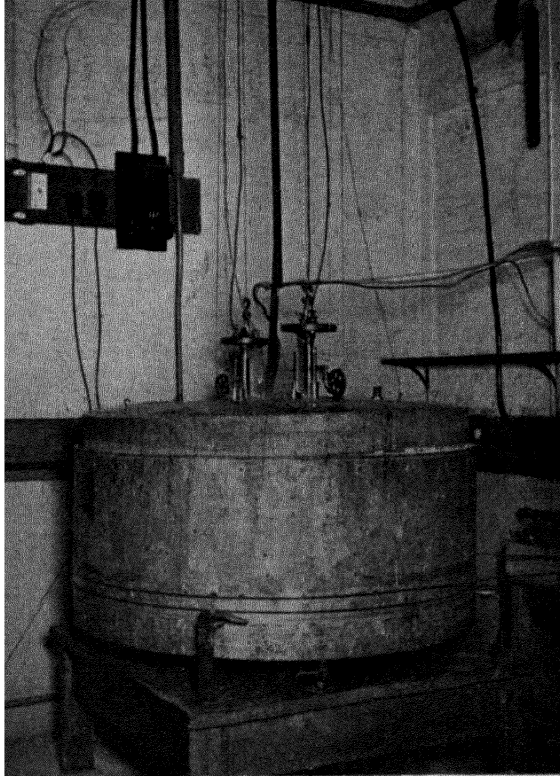
In this way fairly complete information may be obtained on a series of standards. Afterwards all tests are made by comparing the new paint against one of the standards, the performance of which is known not only from the tests just mentioned but also by its behaviour in use, for presumably there

will have been reports from the customers to whom the paint has been sold.

Nature and Size of Test Panels.

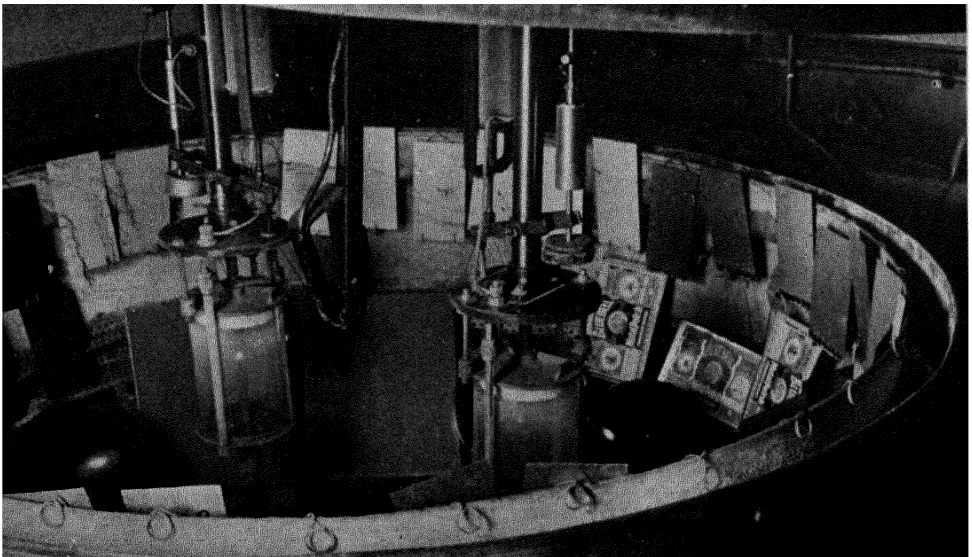
The three most widely used materials for constructing paint weathering panels are wood, black iron and stainless steel. On account of expense the latter can only be used for small panels. The writer has used slate with good success.

When wood is employed it will be found that different results will be



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*Fig. 12.—ACCELERATED WEATHERING TANK (1).
Note the method of rotation.*



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*Fig. 13.—ACCELERATED WEATHERING TANK (2).
With the cover raised, showing interior with two carbon arcs and various panels being exposed, testing paints, varnishes, enamels, tin printing lacquers, etc.*

obtained with soft and with hard woods as well as with flat grain and with edge grain. In this country the most severe conditions of exposure are experienced at an angle of 45 degrees facing south and, therefore, all test panels should be exposed in this manner in order to obtain as rapid a breakdown as possible. More severe conditions may be simulated by spraying the panels once daily with dilute salt solution. In order to obviate the presence of the base material as much as possible each panel should carry two films—one the standard and the other the new one which is being compared with the standard.

Accelerated Weathering Tests.

It is inconvenient to wait for months or years in order to obtain results from outside weathering tests, therefore artificial weathering cabinets have been devised to simulate in an intensive fashion the conditions which a panel would experience in a cycle of seasons. Ultra-violet light is one of the most destructive agents known to the organic binding media of ordinary paint films. Therefore all accelerated weathering cabinets possess as one of their major components a source rich in rays from this end of the spectrum, usually a carbon or mercury vapour lamp. The next most destructive influence is probably the expansion and contraction due either to temperature differences or to swelling induced by moisture. Therefore a freezing and a heat-cycle test is usually included, together with a water spray.

Carbon Arc Lamps.

In the cabinet in use at the Paint Research Station at Teddington and illustrated in Fig. 12, the panels are inserted in a four-foot diameter drum rotating very slowly, and undergo the following gruelling cycle of changes, being exposed the whole time to the light of two carbon arc lamps in the centre. Every 20 minutes they are exposed to a water-spray of two minutes' duration, and once in 24 hours are frozen for two hours, while one hour of the day is set aside for examination and report. 1,000 hours is a normal time of exposure and is considered very approximately equivalent to three years.

It should be emphasised that no accelerated weathering cabinet can give

more than an indication as to the behaviour of a paint. It can be said that, if one material behaves very much better in the cabinet than another, it will probably under working conditions also be superior and stand up longer. In other words, the test is not definitely quantitative.

The Analysis of Paints.

The first step is the isolation of the pigment. This is done by thinning the paint with a suitable solvent or diluent, followed by sedimentation, filtration or centrifuging.

A medium which will not induce suspension of the pigment on the one hand, nor precipitation of the medium on the other, is necessary. A mixture of ether, benzene, methyl alcohol and acetone has been recommended, while the addition of a little ferric chloride will often cause flocculation in an obstinate pigment.

Identification of Pigment.

The identification of the pigment is usually a simple matter performed by the ordinary method of inorganic qualitative analysis, aided by the colour and a microscopic examination. Dyestuff lakes may be recognised by the methods set out by Green.

Volatile Solvents.

Volatile solvents are isolated by steam distillation on a separate portion of the paint, without removal of the pigment. The aqueous layer should be examined for any likely water-soluble solvents, e.g., alcohols (such as butyl alcohol) or ketones (acetone) by the usual methods.

Water-Insoluble Matter.

The water-insoluble volatile matter is usually quickly identified as to the main constituents by odour. This is facilitated by rubbing a little quickly in the palms of the hands and endeavouring to recognise the constituents by smell as they evaporate. Failure of this test necessitates fractionation and a detailed examination.

Test for Nitrogen.

The residue in the retort is tested for (a) nitrogen, the presence of which indicates the probable presence of urea resins or nitrogen-containing catalysts; (b) sulphur, the presence of which indicates the presence of sulphurised oils, and (c) chlorine, the presence of which indicates

the presence of vinyl resins, chlorinated phenol resin, or chlor rubber or chlor wax. This residue is saponified and a series of steps is then taken for the isolation and identification of various radicles, varying in complexity according to the amount of precision required by the analysis and the ease with which the different compounds may be recognised.

PAINT REMOVERS.

In days gone by when it was necessary to remove paint from a surface, this was always done by burning off with a blow-lamp. Later caustic substances were employed to saponify the oils, when the paint film could then be readily stripped. Caustic soda attacks the cellulose of wood and, unless properly neutralised with, for example, acetic acid, is dangerous, as it is liable to attack subsequent coats. In recent years neutral paint and varnish removers have been manufactured on a large scale and find extensive use.

Modern Type.

The modern type of paint remover contains a substance such as benzol, capable of dissolving a waxy material, and another solvent miscible with it in which the wax is comparatively or entirely insoluble, e.g., alcohol or acetone. The function of the wax is to form a film which retards the evaporation of the volatile solvents and allows them time to attack the underlying film. In addition, the wax acts in a semi-mechanical way, giving a viscous and highly thixotropic mixture which does not readily run off vertical surfaces.

To prevent spontaneous crystallising out of the wax during storage it is a common practice to add a small amount of nitrocellulose or of dry soap.

Cellulose.

Some manufacturers replace the whole of the wax by nitrocellulose, which,

roughly, can be made to perform the functions just mentioned. Cellulose, however, in general does not work nearly so well as wax. A small amount is not harmful, but when employed in excess it increases the viscosity so much that the action of the remover is slowed to a great extent.

All old paint and varnish films are porous, and the more mobile a paint remover the more quickly it can penetrate the film. High viscosity hinders this penetration. Hence, to prevent clogging, only the minimum amount of wax and/or cellulose should be used.

Few paint removers actually dissolve the coating to which they are applied. They merely soften and loosen it to such an extent that it may be subsequently stripped with ease. Since in any homologous series the ability to disperse a colloid varies inversely as the molecular weight, the lightest and most volatile solvents are the most efficient.

Formula for Paint Remover.

An excellent paint remover can be made as follows :—

Acetone	20 per cent.
Methyl acetone ..	37 " "
Benzol	40 " "
Ceresin	3 " "

"Methyl acetone" is a commercial product which, in addition to acetone (dimethyl ketone), contains methyl alcohol and methyl acetate.

Another Formula.

Another formula consists of the following :—

Mesityl oxide	2 gal.
Benzol	5 "
Ethyl acetate	3 "
Nitrocellulose	$\frac{1}{4}$ oz.
Paraffin wax	3 $\frac{1}{2}$ lbs.

Mesityl oxide is 4-methyl 3-pentenone 2, $(CH_3)_2C=CH.CO.CH_3$. It occurs in acetone oil.

THE CHEMISTRY AND PHARMACY OF VEGETABLE DRUGS

PART XII.—ALKALOIDAL DRUGS. 6. Coca, etc.

By NOEL L. ALLPORT, A.I.C.,

Assistant Analyst, The British Drug Houses, Ltd.

COCA, "the divine plant of the Incas," has been cultivated in Peru and Bolivia for many centuries. The native Indians chew the dried leaves of the shrub after mixing them with slaked lime or plant ash, and thereby allay the onset of hunger and temporarily derive increased powers of physical endurance.

The leaves from three varieties of the plant are employed commercially. Truxillo, or Peruvian coca originates from *Erythroxylum truxillense* and consists of dried pale green leaves 3 to 6 cm. long and 2 to 3 cm. broad. The brownish-green Bolivian coca leaves, from *erythroxylum coca*, may be 4 to 8 cm. long and 2.5 to 4 cm. broad, but smaller leaves are common. On the upper surface of both varieties the midrib lies in a slight depression, while on the under surface two curved lines run from the base to the apex of the leaf on either side of the midrib. These features, which are quite obvious in the Bolivian drug, are not so strongly marked in the leaves of truxillo coca.

When the epidermal cells of the under surface are examined microscopically they are seen to project in the form of papillæ, which in surface view appear as circular rings. This important diagnostic characteristic is illustrated in Fig. 2. *Erythroxylum coca* is also cultivated in Ceylon and Java. The plant used in the latter country is a special variety (*spruceanum*, Burck), and it is richer in alkaloid than the drug grown in other countries.

Chemistry of Coca.

The leaves contain several alkaloids derived from ecgonine, the most important of which is cocaine. The other alkaloids include cinnamyl-cocaine, α -truxilline, β -truxilline, isatropyl-cocaine and benzoyl-ecgonine. The percentage of total alkaloids present in the commercial leaves varies from 0.1 to 2.4, Java coca containing the highest amount, consisting largely of cinnamyl-cocaine. Truxillo leaves generally contain more alkaloid than the Bolivian drug, but only about one half is cocaine, whereas this alkaloid may constitute three-fourths of the total bases yielded by the material from Bolivia.

When cocaine and the above-mentioned associated alkaloids are hydrolysed by heating with dilute hydrochloric acid they all yield ecgonine, which is a carboxylic acid derivative of tropine, one of the hydrolytic products of atropine (see Vol. 3, page 846). Cocaine itself is benzoyl-methyl-ecgonine, and its relationship to ecgonine is clearly expressed in the following formulæ.—

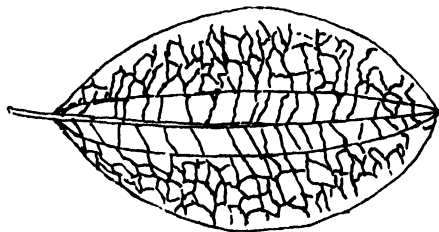
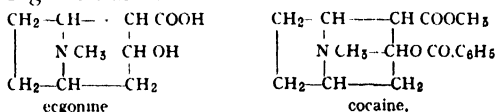


Fig. 1.—COCA LEAF.

This shows the venation of the under-side of the Bolivian leaf. Note the prominent lines on each side of the midrib.

Another alkaloidal substance of some importance is found in coca, particularly in that from Java, called tropacocaine. On hydrolysis this forms benzoic acid and pseudo-tropine, a stereo-isomeride of tropine.

Besides the alkaloidal constituents, the drug contains glucosidal

substances and a tannin termed cocatannic acid, but these are of little relative significance.

Assay of Coca.

The alkaloids contained in coca are soluble in petroleum ether, and this solvent may conveniently be used for the preliminary extraction. The assay can be conducted on the normal principles of extraction and need only be indicated in outline, since the details have already been sufficiently explained in previous articles dealing with alkaloidal drugs.

Fifteen gm. of the powdered drug is macerated with 150 ml. of petroleum ether for 10 minutes, 1 ml. of dilute ammonia is then added, the mixture shaken at intervals during two hours, and the drug agglomerated by the addition of about 15 ml. of water. The supernatant liquor is filtered through a plug of cotton wool, 100 ml. (equivalent to 10 gm. of the drug) transferred to a separating funnel and extracted in the usual way with several portions of dilute hydrochloric acid. The acid extracts are washed with ether to remove fatty

material, then mixed together and rendered alkaline with ammonia and the alkaloids extracted with ether. The alkaloidal residue left after evaporating the ether is dried at 80° C. and determined by dissolving in a measured volume of decinormal acid and titrating back with decinormal alkali, using methyl red as indicator.

Each ml. of decinormal acid is equivalent to 0.030318 gm. of total alkaloid calculated as cocaine.

Pharmacy of Coca.

Galenicals made from the leaves were at one time used as ~~ants~~ during convalescence, but the ~~now~~ rarely

prescribed, owing to the grave risk of inducing a craving for the drug. The liquid extract is prepared by percolating the powdered coca leaves with 60 per cent. alcohol, then evaporating the percolate to low bulk at a temperature not exceeding 80° C. The supernatant liquor is poured off from the precipitate which forms, and the latter washed with water, the washings being added to the clear liquor; the strength of the preparation is then determined by alkaloidal assay and finally adjusted by further evaporation, or dilution with 60 per cent. alcohol. This preparation should contain 0.5 per cent. of total alkaloids. This preparation should be miscible with water.

Elixir and Wine of Coca.

One part of miscible liquid extract, diluted to 6 parts with simple elixir, forms elixir of coca. Simple elixir consists of 40 parts of syrup and 7.5 parts of tincture of orange diluted with water to 100 parts. Coca wine is made by diluting 1 volume of elixir to 8 volumes with sherry which has been detannated by maceration with gelatin.

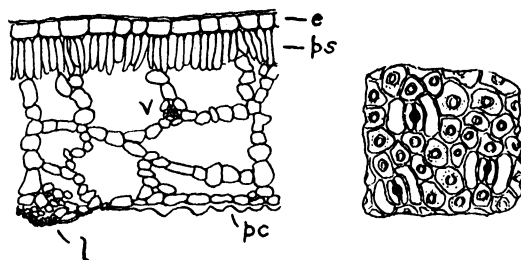


Fig. 2.—HISTOLOGICAL STRUCTURE OF COCA LEAF, HIGHLY MAGNIFIED.

The left-hand diagram shows a transverse section of a Bolivian leaf: (e), upper epidermis of leaf; (ps), palisade cells; (v), veinlet; (l), line on under surface which runs alongside the midrib; (pc), papillose cells of lower epidermis. The right-hand figure is a surface view of the lower epidermis showing the papillose cells which appear under the microscope as circles. The dark structures are stomata.

COCAINE.

Coca is mainly employed as a source of cocaine, which, despite its numerous synthetic rivals, is still one of the most important local anæsthetics used in medicine. In order to save freight and to eliminate the risk of deterioration to which the leaves are subject, the alkaloids are generally extracted in the country of origin and imported into Europe under the name of "crude cocaine." The greater part of the crude material used to-day is prepared in Java and largely consists of the cinnamyl derivative.

Isolation of Crude Cocaine.

The dried and powdered leaves are

mixed with about 5 per cent. of slaked lime and sufficient water to form a paste.

The mixture is extracted with high-boiling petroleum at a temperature of 80° to 100° C. in an iron vessel provided with a steam jacket and stirring apparatus; after separation, the petroleum is agitated with dilute hydrochloric acid and the separated aqueous liquor is neutralised and evaporated to dryness, leaving a residue of alkaloidal hydrochloride.

Alternatively, the acid liquid is rendered alkaline with sodium carbonate and the precipitated alkaloidal bases separated and dried.

Preparation of Pure Cocaine.

The crude alkaloid is now hydrolysed to ecgonine by heating in an autoclave for an hour at 150° C. with a 0.2 per cent. excess of hydrochloric acid. On cooling, the liberated benzoic, cinnamic, and truxillic acids are removed by extracting with an organic solvent and the aqueous liquor evaporated to dryness, leaving impure ecgonine hydrochloride. Pseudotropine hydrochloride, derived from tropacocaine, may also be present.

After washing the product with alcohol, the base is isolated by treatment with sodium carbonate and extraction, after drying, with hot alcohol; it is finally purified by recrystallisation.

The purified ecgonine is now methylated by heating with methyl alcohol and hydrochloric acid, and the methyl-ecgonine is extracted with chloroform and purified by distillation under greatly reduced pressure. Finally, the methyl-ecgonine is converted to benzoyl-methyl-ecgonine (cocaine) by dissolving it in benzene and boiling the solution under a reflux con-

denser with a slight excess of benzoyl chloride. The cocaine hydrochloride, which separates on cooling, is finally converted to the base by treatment with alkali and extraction with chloroform, and purified by recrystallisation from alcohol. The hydrochloride is then re-formed and further purified by recrystallisation from mixtures of alcohol and petroleum ether. In this manner all the alkaloids of coca, except tropacocaine, are converted into the medicinally important cocaine.

Properties of Cocaine and its Hydrochloride.

Cocaine alkaloid occurs as colourless, odourless, monoclinic prisms which melt at 98° C. It is almost insoluble in water, but dissolves in oil and the common organic solvents. The taste is bitter and is followed by a sensation of tingling and numbness in the mouth.

In appearance the hydrochloride superficially resembles the base, and consists of an odourless crystalline powder or small transparent crystals. It is very soluble in water, slightly soluble in chloroform but insoluble in oil and ether. When determining the melting point the capillary containing the sample should not be inserted in the heating bath until the temperature has attained 193° C.; under these conditions cocaine hydrochloride melts at 197° to 199° C.

Tests for Cocaine.

One of the most characteristic tests for cocaine is the formation of violet rectangular plates on treatment with potassium permanganate solution. About 0.1 gm. of the base is dissolved in just sufficient decinormal hydrochloric acid to form a neutral solution. A little alum solution is

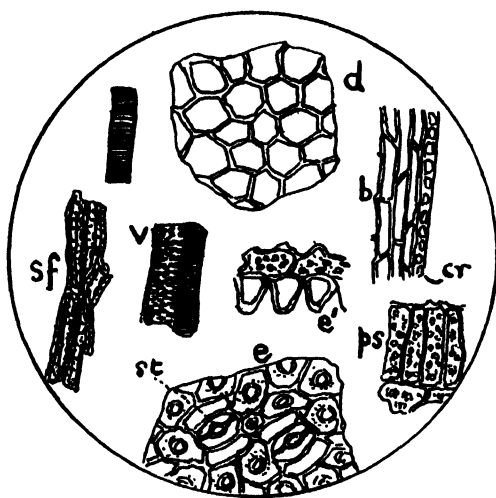


Fig. 3—POWDERED COCA LEAF SHOWING ISOLATED HISTOLOGICAL ELEMENTS ($\times 240$).

The characteristic papillose cells of the lower epidermis are shown at (e) in surface view and at (e') in section; (st), stomata; (sf), sclerenchymatous fibres; (v), fragments of vessels from midrib; (d) upper epidermis; (b) bast, (cr), crystals of calcium oxalate; (ps), palisade cells.

added, followed by 1 per cent. aqueous potassium permanganate; on stirring, the characteristic violet crystals are formed, which are easily seen under the microscope.

The absence of isotropyl - cocaine in cocaine hydrochloride is confirmed by dissolving 0.1 gm. in 100 ml. of water, adding a trace of ammonia, and scratching the sides of the containing vessel with a glass rod. A crystalline precipitate of cocaine should be produced, while the supernatant liquor remains free from turbidity. This is known as Maclagan's test. An acidified aqueous solution should not readily decolorise when treated with a drop of dilute potassium permanganate, thus indicating the absence of cinchamyl-cocaine.

Pharmacy of Cocaine.

The drug is mainly employed in surgical and dental practice to produce localised anæsthesia, for which purpose sterile solutions of the hydrochloride are generally most convenient; these often contain a trace of adrenaline hydrochloride in order to constrict the capillaries at the site of



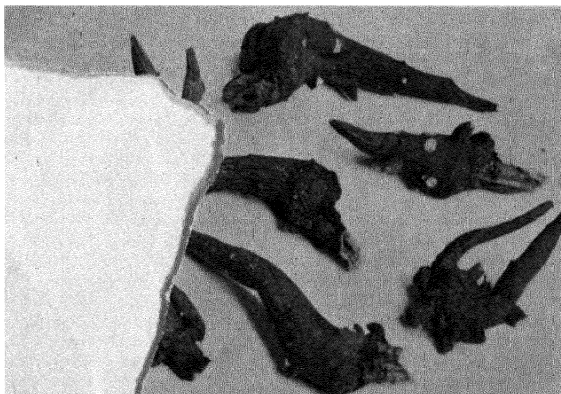
Fig. 4.—EUROPEAN ACONITE ROOT.
Aconitum Napellus. The roots usually vary from 5 to 10 cm. in length, while the upper end may be about 2 cm. in diameter. It contains the exceedingly poisonous alkaloid aconitine.

most valuable medicine for the relief of severe coughs due to irritant conditions of the throat. The preparation of this galenical has already been described in the account of krameria (Vol. II, page 648).

Coca Leaves From a Pre-Incan Grave.

In concluding our account of this drug, reference may be made to an investigation conducted in 1930 by C. Olive Griffiths in the Pharmacognosy Research Laboratory of the Pharmaceutical Society of Great Britain on some coca leaves obtained from the pre-Incan necropolis of Nasca, situated in a desert 150 miles south-east of Lima, the capital of Peru. These leaves,

which were in an excellent state of preservation, were contained in a small bag attached to the mummy pack, and there seems to be little doubt that they were deposited in the grave long before the commencement of the Christian era. The drug was found to contain traces of alkaloidal



are generally smaller than the European and contains the alkaloid japaconitine which is different from aconitine, but is not identical with, aconitine.

material, although the presence of cocaine itself could not be established. Histological examination of the leaves revealed that their cellular structure, even to the smallest details, was the same as that found in the Peruvian variety growing to-day. Nature, in evolving her multitudinous species of living things, bides her time, and the millenniums of our antiquity "are but as an evening gone."

ACONITE.

Aconitum Napellus is a perennial herb which grows wild in Central Europe and is cultivated in England as a garden plant and, commercially, for its medicinal qualities. The plant is often called monkshood, in allusion to the cowl-shaped posterior sepal of its blue flower, while the popular name, wolfsbane, refers to its use on the Continent for poisoning meat bait intended for the destruction of wolves. The root, which is the part of the plant used medicinally, consists of dark brown longitudinally wrinkled conical pieces crowned by an aerial stem (Fig. 4). Another species of aconite which is grown in Japan, *Aconitum uncinatum*, var. *japonicum*, is now extensively employed in place of the European species (Fig. 5). The drug has a slight taste, which is followed by a characteristic sensation of tingling and numbness in the mouth, lasting for some time.

Chemistry of Aconite.

Three alkaloids are known to occur in the drug, of which the most important is the crystalline substance aconitine (acetylbenzoyl-aconine), $C_{34}H_{47}O_{11}N$. Aconitine is intensely poisonous and even 1/300 of a grain taken orally is sufficient to induce distinct symptoms in man. The other alkaloids are amorphous, piraconitine (benzoyl-aconine) being much less toxic

than aconitine, while aconine has little physiological action. The amorphous alkaloids are insoluble in ether, but aconitine dissolves readily. The proportion of aconitine in the European drug ranges from 0.2 to 0.5 per cent. The Japanese root is stated to contain japaconitine, an alkaloid closely resembling aconitine, but not identical with it. The total alkaloidal content of this species is somewhat higher than that of *Aconitum Napellus*.

Assay of Aconite.

For some obscure reason, the content of ether-soluble alkaloid, as determined by chemical methods, does not appear to give a satisfactory indication of the physiological potency of this drug. The United States Pharmacopœia includes a biological assay in which the lethal effect of the sample is tested with guinea pigs. This authority directs that when a 1 in 10 tincture of the root, made by the percolation process, is administered subcutaneously to guinea pigs, the minimum dose that kills two-thirds of the animals shall not be less than 0.0004 ml. per kg.

body weight. This type of assay is an attempt to measure the physiological effect of the drug. The relative

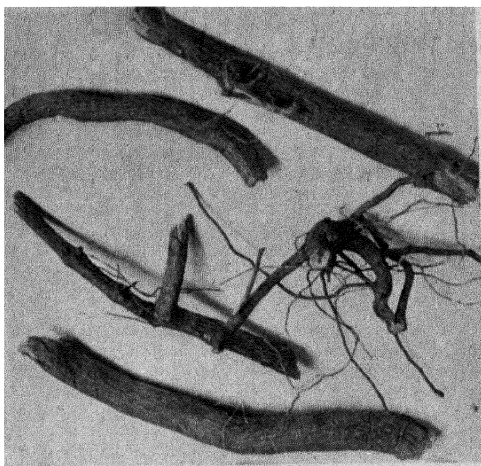


Fig. 6.—GELSEMIUM RHIZOME.

The illustration shows both aerial stems and roots attached to the pieces. The rhizomes are hard and woody. The drug has a bitter taste and a slight aromatic odour.

Pharma

Owing to its abundance, the use of doses of aconite is employed as common orders. It is be regarded

containing 3 per cent. of camphor, is used as an external application for the treatment of neuralgia and acute rheumatism.

GELSEMIUM.

The yellow jasmin, *Gelsemium nitidum*, is a climbing plant indigenous to the Southern United States; it should not be confused with the entirely different yellow-flowering jasmin cultivated in Britain. The rhizome, which constitutes the drug, consists of purplish-brown, approximately cylindrical pieces about 15 cm. long and 0.5 to 2 cm. in diameter, to which rootlets and aerial stems are attached. The purple colour is produced by a network of lines, the intervening areas being yellowish-brown.

Chemistry of Gelsemium.

The drug contains from 0.2 to 0.7 per cent. of alkaloidal material consisting of at least two substances, namely, gelsemine, obtainable in crystalline form, and gelseminine, which is apparently amorphous and possesses much greater physiological potency than gelsemine. Besides the alkaloids, gelsemium root contains β -methyl- α -esculin, which exhibits an intense bluish-green fluorescence in alkaline solution; α -esculin itself is a fluorescent substance which occurs in the bark of the horse chestnut tree. The drug also contains

about 6 per cent. of fixed oil and approximately 4 per cent. of resinous material.

Assay of Gelsemium.

The analytical study of gelsemium is likely to be stimulated in the near future by reason of the recent proposal of the Poisons Board to include preparations containing more than 0.1 per cent. of gelsemine, or of gelseminine, in Part I of the list of poisonous substances. Hitherto but little attention has been paid to this subject, but the alkaloidal content of the powdered rhizome might be assayed by the method described for coca, using a mixture of equal volumes of chloroform and ether in place of petroleum ether, for the initial extraction.

Pharmacy of Gelsemium.

The drug is mainly employed, in association with the bromides and tincture of *cimicifuga*, as an analgesic in the treatment of neuralgia, toothache, and rheumatism; but owing to its liability to produce disturbances of vision and other symptoms of poisoning, it is not very frequently prescribed. Gelsemium has been omitted from the British Pharmacopœia 1932, but the drug and tincture were included in the previous edition (1914). Tincture of gelsemium is a 1 in 10 preparation made with 60 per cent. alcohol by the standard percolation process (see Vol. I, page 13).

PETROLEUM AND ITS PRODUCTS

PART VI.—THE TESTING OF KEROSENE (Continued)

By F. N. HARRAP, M.Sc.

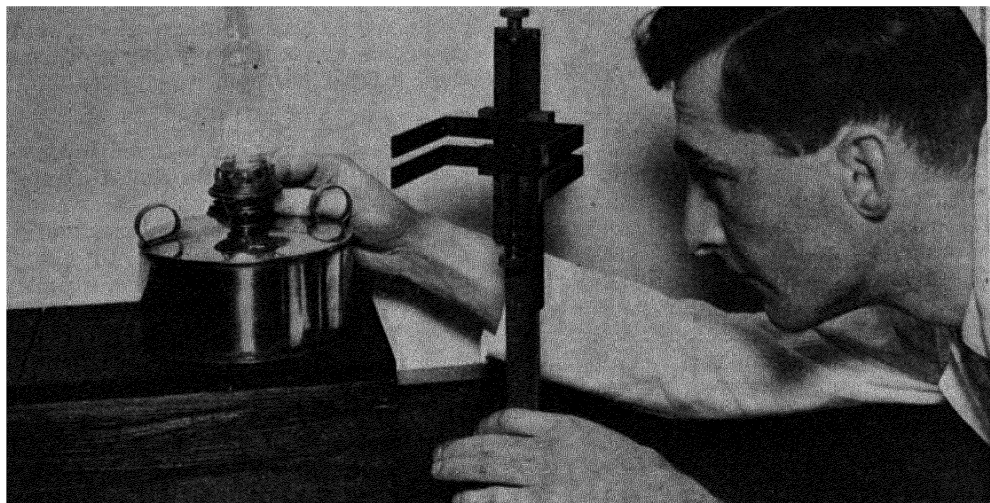


Fig. 1—THE BURNING TEST FOR ILLUMINATING KEROSENES (1)

The sample is burned in a lamp of standardised dimensions, with a flame of standard size. At the end of a 24-hour burning period observations are made of the consumption, the condition of the lamp glass and of the char on the wick. The operator is here seen adjusting the size of the flame after the preliminary one hour burning period.

Doctor Test.

IT has already been pointed out (page 352) that the Doctor Test is applied to gasolines in order to detect the presence of certain undesirable sulphur compounds. The same test can usefully be applied to samples of illuminating kerosene, the details of the test being the same as already described for gasoline testing.

Burning Test.

Large quantities of kerosene are still used for illuminating purposes even in this country, and naturally the best method of assessing the value of an illuminating kerosene is to carry out actual burning tests under carefully controlled conditions. The ideal test would be one carried out

in a lamp representing an average of all the many types used in practice, but since these lamps differ so considerably in type it is impossible to do anything more than adopt some standard method which approximates as closely as possible to this ideal. A standard burning test has been published by the A.S.T.M. (Method D. 187-30) but the I.P.T. have not yet issued a method. The test which will be described is one which the writer has found to give results very closely in line with those obtained in actual practice, and this is undoubtedly the final criterion by which the suitability or otherwise of a test must be judged.

The Apparatus.

The lamp and lamp glass used for the

test are shown in Fig. 1, the container of the lamp having a diameter of $6\frac{1}{2}$ in. and height 3 in. The amount of sample required for a test is approximately 900 c.c., this being appreciably less than is required by other published burning test methods, and this factor is a decided advantage in the investigation of complaints when it is often difficult to obtain a large sample for examination. The lamp glass is $7\frac{1}{4}$ in. in length and varies in diameter from $1\frac{1}{4}$ in. (at the top) to $2\frac{1}{8}$ in. It is not proposed here to specify all the dimensions of the apparatus (which can be obtained from the Lamp Manufacturing Company, of City Road, London), but it is important to check up these dimensions before putting the apparatus into service. The wick employed is the Morgan Crossley $\frac{3}{4}$ -in. paraffin flat wick, ordinary quality, Close N.

Preparation of Wicks and Lamp Glasses.

Before carrying out a test a piece of new wick, at least 7 in. in length, must be dried in a steam oven, soaked in the sample under test whilst still hot, and inserted in the wick holder. If the lamp glass used for the test is an "aged" glass, i.e., it has been used for several previous tests, it is only necessary to clean it with a test tube brush in running water, rinse it with distilled water and dry it in a steam oven. If, however, only new glasses are available these must be aged before being put into service. New glasses, owing to the presence of alkaline compounds, tend to give a very much more intense white bloom than do aged glasses under comparable conditions, and with the same samples, and they must

be treated in the following manner:—

The glasses are immersed for 24 hours in a dilute hydrochloric acid solution (50/50 acid/water), cleaned with a test tube brush, rinsed thoroughly with distilled water and then dried. Subsequently they are used for three 24-hour periods before being passed out for general laboratory use.

The Method of Test.

Before starting a burning test it is most essential that the burner is thoroughly clean, all pieces of char being removed, and care taken to ensure that the air holes and ducts are quite clear. The lamp container is rinsed out two or three times with a little of the sample under test, and is completely emptied before filling up with the test sample. The minimum temperature of the laboratory during the test should not fall below 60° F., and if more than one test is made at a time the lamps should be placed at least 2 ft. apart, and at least 2 ft. from any wall. It is essential to prevent draughts and if necessary a suitable screen of diameter about 18 in. should surround the lamps.

After rinsing the container 900 c.c. of the sample is filled into the lamp and the burner with its wick and lamp glass are fitted in position. The dome (with lamp

glass attached) is then folded back and the wick carefully trimmed with a sharp pair of scissors, so as to obtain a flame 1 in. in height and 1 in. in width, smooth and symmetrical and free from peaks and ears.

The correct height is easily obtained by turning the wick up or down, and the proper width by trimming the corners of the wick. The measurements

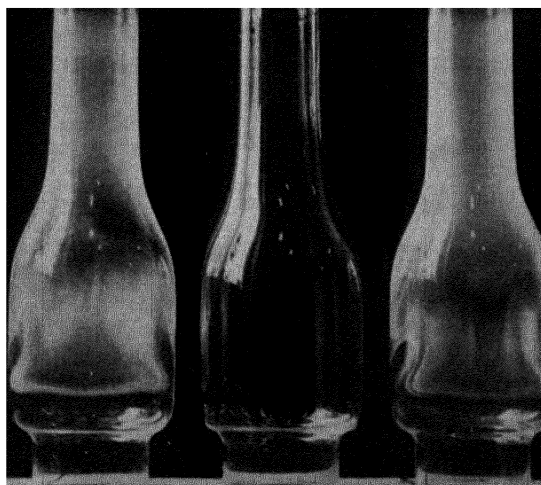


Fig. 2.—THE BURNING TEST FOR ILLUMINATING KEROSENES (2).

This photograph shows typical examples of a very good and of very bad lamp glasses after the 24-hour burning test. The centre glass shows practically no deposition of film, but the others exhibit a heavy white bloom.

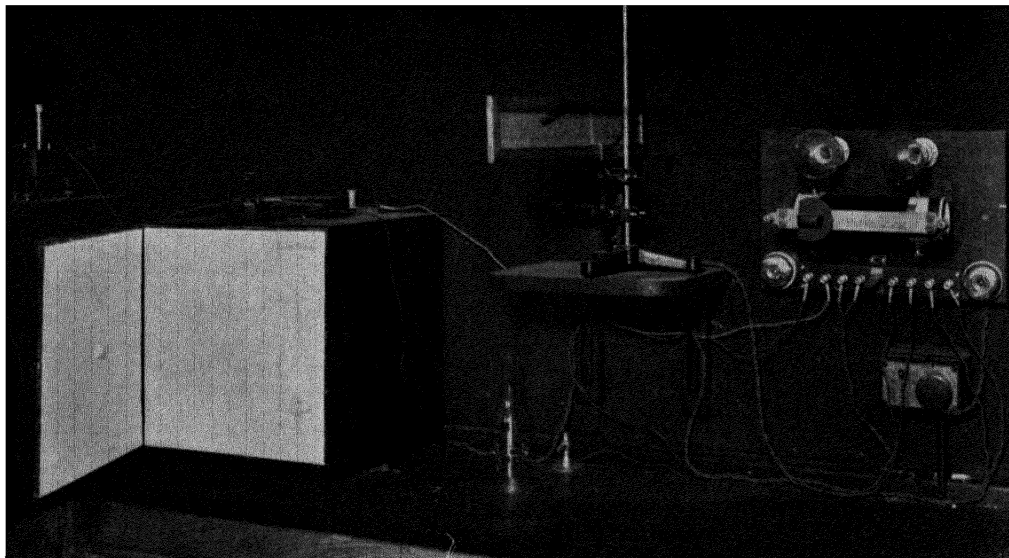


Fig. 3—THE BURNING OR ILLUMINATING KEROSENES (3)

The amount of film on the glass is determined in this apparatus by integrating (by means of a photo-electric cell) the light passing through the lamp glass from a small electric bulb placed inside the glass. The amount of film is expressed as the percentage loss of light as compared with the amount of light passing through a clean glass of the same type.

of height or width (which should be within $\frac{1}{8}$ in. of the standard dimensions) are best obtained by means of a Rather burning test gauge (see Fig. 1). The lamp is allowed to burn for one hour and the flame is then readjusted, if necessary, to the standard height.

No further adjustment is made for the remaining 23 hours during which the flame burns continuously, the total test thus extending over a 24-hour period. At the conclusion of the test the volume of kerosene remaining in the container is measured, so that the "consumption per hour" during the test can be calculated.

Estimation of the Char Produced.

From the charred end of the wick a piece approximately half an inch long is cut off and placed in a small beaker, together with any small pieces of char which may have become detached from the wick during the test. The contents of the beaker are carefully washed by decantation with petroleum ether, care being taken to ensure that all the char is retained in the beaker.

The beaker and contents are dried in an oven at a temperature of 105-110° C. for half an hour, and the char is then removed mechanically from the wick by means of a

spatula or similar convenient instrument. The char must be only that portion which can be removed easily from the wick without cutting or removing unburned wick, and after being collected on a watch glass this char is weighed and the results expressed as "milligrams char per litre of kerosene burned." A first quality burning grade kerosene may give as little as 2 or 3 milligrams char per litre, whilst some of the very inferior "pirate grades" give figures as high as 100 milligrams per litre.

Condition of the Lamp Glass.

The amount of bloom produced on the lamp glass during a burning test is, in general, proportional to the sulphur content of the sample. It is (as has already been pointed out) heavier with new than with old glasses, heavier at cold than at hot spots, and heavier with a small flame than with a larger one. By using only aged glasses of standard dimensions and flames of standard size it is possible to cut out most of the variables, but even then it is necessary to see that the test is carried out in a well-ventilated atmosphere, free from draughts and from ammonia fumes (these accentuate the production of bloom). Typical examples of the blooms produced

by very good and very bad burning kerosenes are shown in Fig. 2.

Measurement of Film on the Lamp Glass.

The easiest method of measuring the amount of film is by visual inspection of the glass after the test, the intensity of bloom being described as "heavy" "moderate" or "slight," and the colour as "brown," "white," "blue" or whatever the colour may be. This method, as will be appreciated, is not very scientific and is apt to lead to erroneous conclusions when the results given by different laboratories or even by different observers have to be compared.

For example, opinions may differ as to whether a lamp glass showing localised patches of bloom is to be considered as better than, or worse than, a lamp glass exhibiting the same total amount of bloom, but which is more evenly distributed over the glass. In order to cut out the personal element it is preferable to determine the amount of film

by a scientific method, using the integrating photometer method devised by the Anglo-Persian Oil Company and described to the I.P.T. Summer Conference in 1932.

The Integrating Photometer.

The apparatus used for the test is shown in Fig. 3, the amount of light absorbed by the film on the glass being determined by placing a small electric bulb inside the lamp glass and integrating the light passing through the glass by means of a photo-electric cell. The lamp glass is held in a vertical position by a spring clip on a lamp holder and a light aluminium disc

is placed over the top end of the glass to prevent the direct rays of the electric bulb from falling on the photo-electric cell, which is mounted in the centre of the top of the box. Care should be taken to ensure that the V filament of the bulb is so placed relative to the lamp glass that the plane of the filament coincides with that of the flame during the burning test. A suitable type of bulb is the 12-volt, 12-watt gas-filled lamp, whilst the G.E.C. —K.G.7 photo-electric cell has been found satisfactory for the test.

Using the Integrating Photometer.

The method of estimating the percentage



Fig. 4.—BURNING TESTS ON LONG TIME BURNING OILS. The photograph shows the standard types of lamp (Adlake on the left, Welch on the right) used for testing long time burning oils. In this case the test is prolonged for a seven-day period and the lamps are inspected each day.

of light absorbed by the film is by noting the galvanometer deflection with the filmed glass in position, and comparing the reading with the deflection obtained when using a clean glass of the same type. The lamp is switched on for 15 minutes and the zero adjustment is then made with the lamp switched off, the zero being checked with the lamp

on and the galvanometer switched off. By adjusting the resistance a suitable deflection on the scale is then obtained with a clean glass in the spring clip, and a reading is next made with the filmed glass to be tested, the two glasses being alternated until steady readings are obtained.

Calculation of Results.

The amount of light absorbed by the film is expressed as "film (per cent. absorption)" and is calculated from the formula :—

Film (% absorption)

$$= \left(1 - \frac{\text{Film reading} - \text{Zero reading}}{\text{Clean glass reading} - \text{Zero reading}} \right) \times 100$$

The results are repeatable to within 1 per cent., the best burning kerosenes giving figures of 5 per cent. or less, whilst inferior grades give figures of 15 per cent. and over.

Burning Tests for "Long Time Burning Oils." (I.P.T. Method I.T.P.O. 21)

Special burning tests have been devised by the I.P.T. to control the quality of the so-called "long time burning oils," such as are used for signal lamps on the railways. These oils are kerosenes which have been subjected to special refining methods to ensure that they will meet the arduous conditions encountered in service, and they are, as a rule, somewhat less volatile products than the illuminating kerosenes sold for ordinary domestic lamps and heaters. The two lamps given as alternatives by the I.P.T. are the No. 5 "Adlake" Semaphore lamp, fitted with the "Adlake" No. 41 round flame long-time burner, and the Welch lamp, No HS 68, fitted with a Welch burner, Harrison Cone. These lamps are shown in Fig. 4, the "Adlake" lamp on the left, the Welch lamp on the right. Details as to the types of wick employed, and specifications for the burners are given in the I.P.T. method but need not be recapitulated here.

Use a New Wick for Each Test.

It is essential that a new wick should be used for each test, the wick being dried in an oven at 105-110° C. for 30 minutes

and then immersed in the oil to be tested until required for use. As in the case of the 24-hour test for ordinary illuminating kerosenes, the lamps must be burned in a well-ventilated room, free from draughts, and they must not be placed too close to each other or too near to any wall.

The prepared wick is placed in the burner and is trimmed level by means of a straight cut with a razor blade and the lamp is then filled with the oil to be tested. The

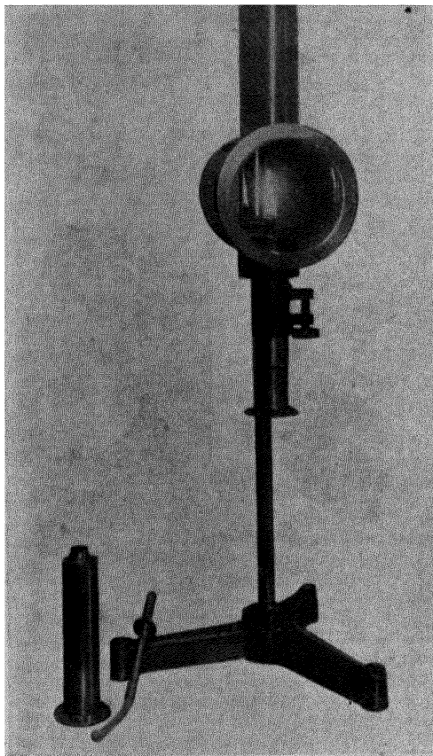


Fig 5—THE SMOKE POINT APPARATUS

This test shows the height at which a kerosene flame can be burned without smoking. The kerosene is burned in a draught-proof lamp of special design, and the maximum height of flame at which the kerosene burns without smoking is read off on a millimetre scale

wick is lit and is turned up to give the maximum flame and after burning for one hour the flame is adjusted to a height of 0.7 inch by means of the gauge attached to the burner or to the fount of the lamp, the zero mark of the gauge corresponding with the top of the burner. After adjusting the flame height to the 0.7 inch mark the lamp is allowed to burn continuously for 7 days, observations being recorded daily. These should include the height of flame, condition of flame, wick and burner and soot formation, if any. At the end of the seven-day test the final observations are made and recorded and the consumption of long time burning oil is ascertained. If a quantitative estimation of the amount of char produced on

the wick is desired this is made by the method already described in this article.

Smoke Point.

This test does not appear in the I.P.T. Method Book, but it has been adopted by the I.P.T. as a standard method. It is intended to indicate the maximum height at which a kerosene flame can be burned without producing smoke, the test being

made in a lamp so constructed as to be unaffected by adventitious draughts.

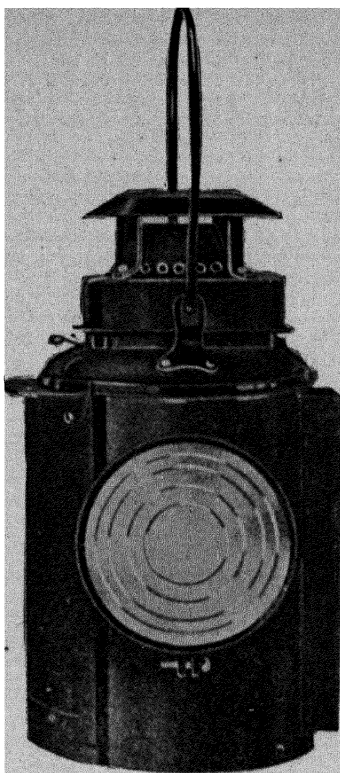
The Apparatus.

The lamp, which is shown in Fig. 5, consists essentially of the holder and lamp of the Weber photometer. It is provided with a reflector by means of which the image of the flame is projected on to an opal glass to which a millimetre scale is attached.

The Method of Test.

The lamp is completely filled with the sample to be tested, and the wick-holder with its wick is screwed on to the lamp. The wick must be clean and must have been extracted with ethyl ether prior to the test, subsequently being saturated with the sample under examination. Any frayed edges, etc., on the wick are removed by trimming with a razor blade. The lamp, after filling, is heated on a water bath to a temperature of about 40° C. to ensure sufficient absorption of the oil by the wick, this being particularly important in the case of kerosenes of relatively high viscosity.

The lamp is then placed in the holder, the wick is lit, and the flame is protected from draughts by the metal lid. The flame is turned up until smoking occurs, and is then turned down gradually until



Griffin and Tallock, Ltd.
Fig. 6.—ANOTHER VIEW OF THE "ADLAKE" LAMP USED FOR TESTING LONG TIME BURNING OILS. Showing the plain glass front.

it no longer smokes, the height of flame being read off on the scale. The raising and lowering of the flame is repeated several times and the average of the various readings taken is recorded as the smoke point.

The higher the smoke point, the smaller is the tendency for the kerosene to produce smoke during burning and, of course, the greater is the height at which the kerosene flame can be maintained in practice without the production of smoke.

Anti-knock Value (for Power Kerosenes).

Where kerosene is used as a fuel in engines provided with spark ignition it must be of high anti-knock value and of good volatility. The determination of anti-knock value is really the province of the engineer rather than of the chemist, and as no one method for checking up anti-knock value has yet been generally accepted it is felt that further discussion of the question would be rather out of place

here. As a matter of interest it may be recorded that the octane rating (see the previous articles on gasoline testing) of ordinary illuminating kerosene varies between say 10 and 25, whilst the kerosenes supplied for power purposes have octane ratings as high as 60 or 65.

INSECT FLOWERS AND DERRIS ROOT

By G. MIDDLETON, B.Sc., A.I.C.,

Assistant Analyst, The British Drug Houses, Ltd.

BEFORE the introduction of organic insecticides the destruction of insect pests had been conducted with mineral poisons of the type represented by lead arsenate. These substances have the obvious disadvantage of being highly toxic both to man and the higher animals, and it was, therefore, natural to seek for insecticides more specifically poisonous to insects. Such substances have now been discovered in certain plants, and extracts of these are being ever more widely used for insecticidal preparations.

Insecticidal Plant Materials.

The most important materials in this class are insect flowers and derris root, both of which contain compounds which are extremely toxic to insects and other cold-blooded organisms, while comparatively harmless to warm-blooded animals. It does not, however, follow that they are equally efficacious against all forms of insect pests; it is only field trials which can decide their relative suitability for a particular purpose. Both insect flowers and derris root are contact poisons and, unlike mineral poisons, it is not necessary for them to be taken into the stomach of the insect to exert their

toxic effect. This means that they can be used against sucking insects which feed on the juices of plants.

Insect Flowers.

Commercial "insect flowers" are the dried flowers of *chrysanthemum cinerariifolium*, a plant which is also known as pyrethrum, though it is not related to the pyrethrum of our gardens or to the plant which furnishes the pyrethrum root used in medicine. Originally the flowers were imported from Dalmatia, but now a good deal is derived from Japan, while experimental cultivation has been carried

out in England and other countries. Empire supplies from Kenya are now becoming available.

Until quite recently, neither chemical nor biological tests were used for standardising the material, and the unexpanded flower buds were considered to be the most toxic, commanding the highest price in the market. Recent work has shown, however, that this view is incorrect, and that the total yield of toxic substances is increased by allowing the crop to become mature before harvesting.

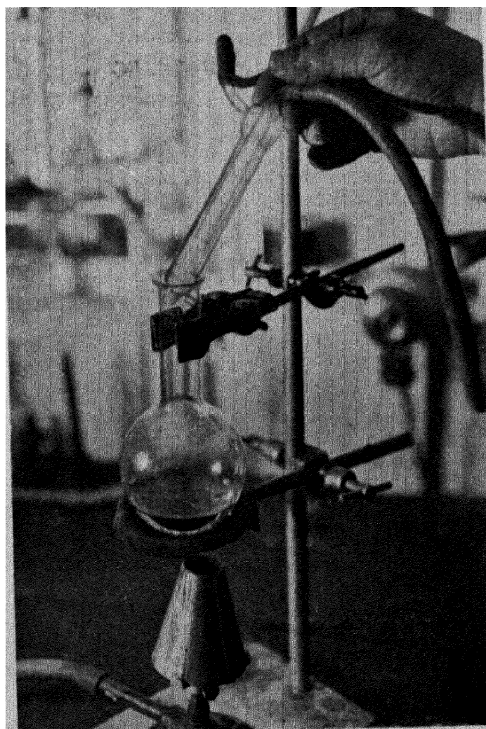


Fig. 1—ASSAY OF INSECT FLOWERS (1)

A simple form of condenser, slipped into the neck of the flask, is used as a reflux during the saponification of the extract

Method of Employment.

The earliest use of insect flowers was

in the form of "insect powder," consisting of the powdered flowers, to which other substances such as borax might occasionally be added. An advance on this type of insecticide is an extract of the flowers in kerosene, employed as a spray. This extract, with the addition of perfume, is the basis of the proprietary fly sprays which now have such a large sale, especially in tropical countries. As the kerosene is injurious to the leaves of plants, preparations which can be diluted with water are

Chemistry of the Toxic Principles.

Pyrethrin I has been shown to be the ester formed by combination of an alcohol "pyrethrolone" with chrysanthemic monocarboxylic acid; while pyrethrin II is the ester of the same alcohol with chrysanthemic dicarboxylic acid monomethyl ester. The very specific nature of the toxic action is shown by the fact that the pyrethrolones and the two acids themselves are not toxic; while of a number of compounds of a similar structure

prepared synthetically, not one approached the toxicity of the natural compounds. It is interesting to note that the dose of pyrethrin I required to kill an aphid has been calculated to be not more than six millionths of a gram. The only known substance which approaches it in toxicity is rotenone (see below).

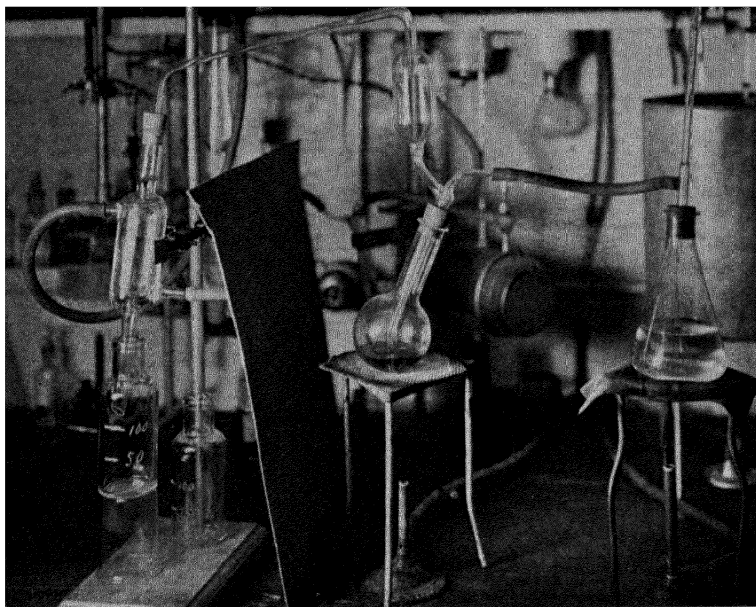


Fig. 2.—ASSAY OF INSECT FLOWERS (2).

Distilling over the chrysanthemic acid in a current of steam. The screen prevents petroleum ether vapour coming in contact with the flame.

made for agricultural use by mixing an extract of the flowers with emulsifying agents.

The Toxic Principles.

Pyrethrum flowers contain two chemically related toxic substances, known as pyrethrin I and pyrethrin II (these must not be confused with the alkaloid "pyrethrine" present in pyrethrum root), and a satisfactory method of chemical assay based on the determination of the percentage of the first compound has been developed. In addition there is a biological method, based on the determination of the relative number of flies killed by spraying a certain quantity of the material under investigation into a definite volume of air.

The Chemical Assay of Insect Flowers.

Of the two compounds present in insect flowers, pyrethrin I is several times as toxic as pyrethrin II. It is, therefore, usually sufficient to determine the content of pyrethrin I only, though both constituents may be determined if required. The method is based on the saponification of the extractive material obtained from the flowers, followed by acidification and distillation in steam.

The residue contains the chrysanthemic dicarboxylic acid from the pyrethrin II, while the chrysanthemic monocarboxylic acid from the pyrethrin I distils over, and is determined by titration with standard alkali after separation from other volatile acids by

extraction with petroleum ether.

Method of Assay.

Ten gm. of the powdered insect flowers is extracted with petroleum ether (boiling point 40 to 50° C.) in a continuous extraction apparatus. (In order to avoid transference of the solution at later stages of the analysis, it is convenient to use for the extraction a long-necked flask of 350 c.c. capacity.)

When the extraction is complete, as shown by the complete removal of colouring matter from the material, the extractor is removed from the flask, and the petroleum ether solution, which should have a volume of about 50 c.c., is treated with 0.2 gm. of caustic soda (in pellets) and 5 c.c. of pure methyl alcohol. A condenser is attached to the flask, and the mixture is refluxed vigorously for two hours in order to saponify the pyrethrins. The condenser is then removed and excess (about 15 to 20 c.c.) of N/1 sulphuric acid is added.

Steam Distillation.

The flask is now fitted up for steam distillation as shown in the illustration, with a still head attached direct to a condenser without any rubber connections. For use as receivers, two bottles are marked with grease pencil at the 50 and

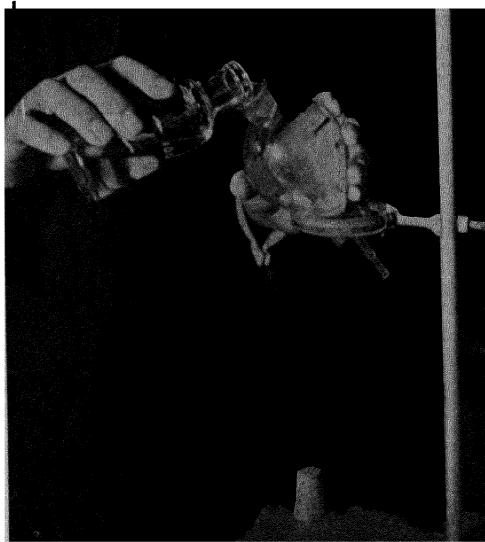


Fig. 3.—ASSAY OF INSECT FLOWERS (3)
Transferring the first portion of distillate to a separating funnel for the shake-out

100 c.c. levels. A gentle current of steam is passed into the flask, driving over the petroleum ether (care must be taken that the latter does not distil so rapidly that uncondensed vapour comes out of the condenser, with consequent risk of fire, and the receiver should be screened off from the flame).

When all of the petroleum ether has been distilled over, a rapid current of steam is passed and at the same time a small flame is placed under the flask containing the mixture and adjusted so that the volume of liquid in this flask at the end of the distillation is about 20 c.c. When 50 c.c. of aqueous distillate has collected below the petroleum ether in the first receiver, the receiver is changed and a further 50 c.c. is collected.

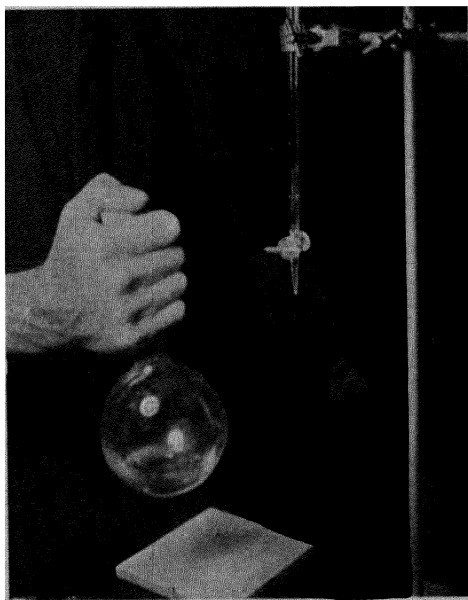


Fig. 4.—ASSAY OF INSECT FLOWERS (4)
During the titration vigorous shaking is necessary in order to extract the acid from the petroleum ether.

Transfer Contents of First Receiver to a Separating Funnel.

The contents of the first receiver are transferred to a separating funnel, about 2 gm. of sodium chloride is added to assist separation, and the mixture is shaken vigorously for one minute. The lower layer is then run back into the bottle, and the solution in the funnel is washed with a little water, which is also run out into the bottle.

The petroleum

ether solution is poured off into a flask containing 20 c.c. of previously boiled and cooled water and a few drops of phenolphthalein solution, to which sufficient N/50 sodium hydroxide has been added to produce a distinct pink colour.

The flask is corked (not rubber) and titrated with N/50 sodium hydroxide until a distinct pink colour, not destroyed by vigorous shaking, is produced. It is sufficient to commence by adding 1 c.c. of the alkali at a time until the colour is only discharged slowly, and then quantities of 0.5 c.c.

Return Aqueous Liquid to Separator.

The aqueous liquid which has already been extracted once is returned to the separator and shaken out again with another portion of 50 c.c. of petroleum ether. The lower layer is run off, and the contents of the second receiver are transferred to the separator with the addition of 2 gm. of sodium chloride, the extraction and washing being completed as before.

This petroleum ether solution is added to the titration liquid and the titration completed by the addition of progressively decreasing quantities of the standard alkali until the first pink colour, permanent on shaking, is obtained. One c.c. of N/50 sodium hydroxide is equivalent to 0.0066 gm. of pyrethrin I. Good samples of the flowers should contain at least 0.4 per cent.

Determination in Kerosene Solutions.

If the above method is to be employed for the kerosene solutions used as sprays, it must be modified as follows: 100 c.c. of the solution is hydrolysed with methyl alcohol and caustic soda, as above. The bulk of the kerosene is poured off into a second flask and refluxed with a second quantity of methyl alcohol and soda, the kerosene is poured off again, and excess of sulphuric acid is added. The contents of

the second flask are then transferred to the first one and washed in with 50 c.c. of petroleum ether. The remainder of the determination is completed as before, but a blank (generally equal to about 0.3 c.c. of N/50 alkali) must be allowed for the acids present in the kerosene. The presence of perfume esters may cause the results to be too high.

DERRIS ROOT.

Derris root (tuba root) is the root of *Derris elliptica*, a plant growing in the East Indies. The toxic ingredient is known as rotenone, and is extremely poisonous to cold-blooded organisms such as insects and fish.



Fig. 5.—ASSAY OF DERRIS ROOT—METHOXYL METHOD (1).

Semi-micro apparatus for the determination of methoxyl. (Right to left) Tube from carbon dioxide generator, decomposition flask carrying head with gas washer, double absorption tubes containing bromine solution, and beaker for absorbing bromine fumes.

Rotenone-containing Roots.

Derris is one of a number of plants containing rotenone, of which may be mentioned black and white haiari (a species of *Lonchocarpus*, from Guiana), cubé root (*Lonchocarpus nicou* and other species, from South America), barbasco root and Brazilian timbo root. Many of these are used by the natives for poisoning streams in order to kill the fish. A number of other plants are known to contain rotenone and may become important sources.

Toxic Components.

Rotenone is a crystalline compound, insoluble in water but soluble in organic compounds. It is practically harmless to animals, and one experimenter consumed 0.15 gm. of it without ill effects. At the same time, it is liable to produce irritation of the

skin, and the dust produced when the root is being ground is extremely irritating. It is interesting to note the high proportion (up to 10 per cent.) of this toxic component of the roots compared with the small amount of active principle present in insect flowers.

In addition to rotenone, derris and the other roots contain other compounds. Of these deguelin has a toxicity to insects

about one-tenth that of rotenone, the others still less. In addition, the roots sometimes contain a large proportion of resins which interfere with the crystallisation of the rotenone

Application of Derris and Similar Roots.

Derris is slower in action than pyrethrum, and washes containing both are becoming popular. One of its chief uses is to protect cattle against the warble fly, which burrows in the skin and ruins the hide. Though its active principles are insoluble in water, the powdered root, emulsified with water, forms one of the best methods of application

Assay of Derris.

Derris may be assayed biologically by determining the toxic action on gold fish, but more generally physical or chemical methods of assay are preferred. Of these, three will be described below.

The Methoxyl Method.

Both rotenone and deguelin contain the methoxyl grouping (OCH_3), so that a determination of the methoxyl content of the extract of the root may be used as a measure of the content of toxic ingredients. The method described below is a semi-micro method, due to Viebock and Schwappach, and offers several advantages over the usual method of determination of methoxyl.

Principle of the Method.

By heating a compound containing a methoxyl group with hydriodic acid, methyl iodide is formed and, being volatile, may be carried away in a current of carbon dioxide. By passing this through a solution of bromine in acetic acid, the

methyl iodide is oxidised to iodic acid, which may be determined, after removal of the excess of bromine, by titration with thiosulphate.

The Apparatus.

The apparatus used is shown in the illustration, and consists of a small flask of about 15 c.c. capacity. The head attached to the flask carries a small gas washer and then leads to two absorption tubes. The different parts of the apparatus are connected together by means of ground glass joints.

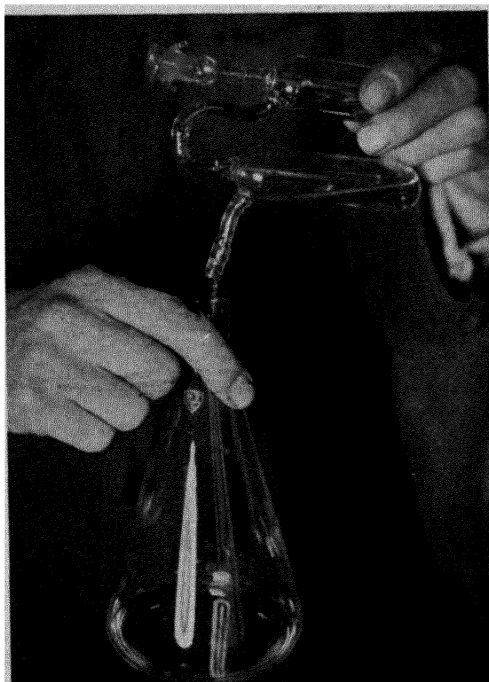


Fig 6—ASSAY OF DERRIS ROOT—METHOXYL METHOD (2).

The contents of the absorption tubes are tipped out quickly into a solution of sodium acetate.

The Methoxyl Determination.

The powdered root is extracted with ether in a continuous extractor, the ethereal solution is transferred to a small beaker and evaporated to dryness. In order to remove all traces of ether, which would interfere with the determination, chloroform is added to the residue and evaporated off again.

About 0.2 gm. of the extract is accurately weighed out into the flask of the apparatus, and a similar quantity of red phosphorus is added in order to remove any free iodine from the hydriodic acid. The flask is then half filled with hydriodic acid (density 1.7), and the head is attached. In the gas washer is placed a mixture of 0.5 c.c. of N sodium hydroxide and 5 c.c. of N/10 sodium thiosulphate, while the absorption tubes contain a solution prepared by dissolving 1.5 gm. of potassium acetate in a very small quantity of water, making up to 15 c.c. with glacial acetic acid, and adding 0.5 c.c. of iodine-free bromine (AnalaR). This mixture is poured into the first tube, when, by tilting, about

one-third of it is transferred to the second one. The outlet from the absorption tubes dips under a solution containing sodium acetate and formic acid, in order to absorb bromine fumes.

Heating the Flask.

The flask is connected to a carbon dioxide generator, and a gentle stream of gas is passed through the apparatus. The flask is heated by means of a micro burner placed a few inches below the bottom of the flask, and adjusted so that vapour is seen to condense in the lower half of the long tube, but does not reach the gas washer. After about one hour, or less, the absorption tubes are disconnected.

Two gm. of anhydrous sodium acetate is dissolved in about 30 c.c. of water in a 600 c.c. conical flask (it is important that no salt should remain undissolved) and the contents of the absorption tubes are run into this solution and mixed rapidly, the tubes being then washed out with water. Formic acid (about 0.5 c.c.) is added drop by drop to the solution until, after standing for a moment, the mixture is just decolorised, and then any remaining traces of bromine are removed by adding a



Fig. 7.—ASSAY OF DERRIS ROOT—CRYSTALLISATION METHOD.

The concentrated carbon tetrachloride solution is cooled in ice before filtering off the rotenone. The small flask immersed in ice contains tetrachloride to be used for washing the crystals.

few drops of a 25 per cent. solution of phenol in glacial acetic acid. After waiting *at least two minutes* after the addition of the phenol, potassium iodide and sulphuric acid are added, and the liberated iodine is titrated with N/10 sodium thiosulphate. One c.c. of N/10 thiosulphate is equivalent to 0.00051706 gm. of methoxyl, or 0.003293 gm. of rotenone.

The Carbon Tetrachloride Method.

This method is based on direct crystallisation of the rotenone from the solution obtained by extracting the root with carbon tetrachloride. The solubility of rotenone in carbon tetrachloride is only 0.4 per cent. at room temperature, so that a fairly good recovery should be possible by concentrating the solution and cooling in ice, but, unfortunately, the resins present in derris root may completely prevent the crystallisation of the rotenone so that in the case of roots containing a comparatively small percentage the method fails entirely. The process is much more satisfactory for cube roots which contain more rotenone and less resins.

The crystals which are actually obtained are not

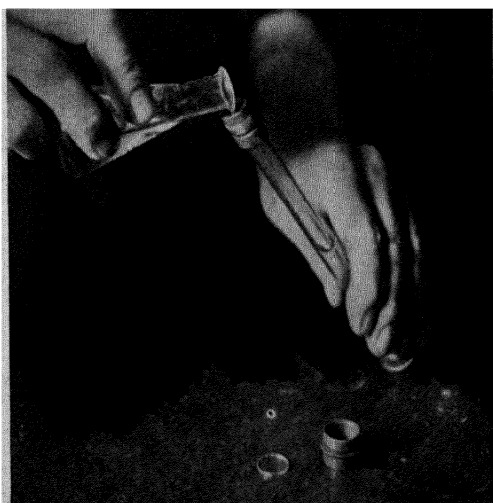


Fig. 8.—ASSAY OF DERRIS ROOT—POLARISATION METHOD.

Filling a polarimeter tube with the benzene extract of the root.

rotenone itself, but a compound of this containing "carbon tetrachloride of crystallisation," which is not lost on exposure to air. The weight obtained must, therefore, be multiplied by a factor in order to give the actual weight of rotenone in them. Even when a fair proportion of rotenone is present, it may be found to be impossible to get the solution to crystallise, even after standing for several days in a cold room. The only certain method of initiating crystallisation in such a case is to add a minute trace of the crystals obtained from a previous determination.

Details of the Method.

Twenty-five gm. of the powdered root is extracted for at least twelve hours with carbon tetrachloride in a continuous extraction apparatus. The extract is transferred to a 50 c.c. beaker, concentrated on the water bath to 12 to 15 c.c., and allowed to cool. If no sign of crystallisation appears on cooling, then it is necessary to "seed" the liquid by stirring with a glass rod, which has been dipped in the crystals obtained from a previous determination and has a little of the crystalline dust adhering to it. The mixture is then allowed to stand overnight to allow the crystallisation to become complete.

The beaker is now placed in a mixture of crushed ice and water for ten minutes, taken out, wiped dry, and the contents transferred to a sintered glass crucible (No. 1 G 4) and sucked dry. The vacuum is turned off, and the crystals remaining in the beaker are washed into the crucible with a few (not more than 5) c.c. of tetrachloride which has also been cooled in ice. The crystals in the crucible are stirred up thoroughly with this fresh portion of solvent before the vacuum is turned on again. The crucible is now placed on its side to dry to constant weight. The weight of the crystals obtained is

multiplied by the factor 0.719 in order to give the weight of rotenone contained in them.

The Polarimetric Method.

Both rotenone and deguelin are optically active, the respective specific rotations in benzene solution being for rotenone $[\alpha]_D^{20} = -233^\circ$, and for deguelin $[\alpha]_D^{20} = -23.2^\circ$. As these values are proportional to the relative toxicities of the two compounds in dilute solution, a determination of the optical rotation of an extract gives a good measure of the toxicity of a sample of root. Danckwortt, Budde, and Baumgarten, who proposed this method, have shown that the results obtained by it are in satisfactory agreement with the percentages of rotenone and deguelin as determined by the elaborate method of Takei and others, while it is equally suitable for roots with a high and a low percentage of rotenone.

Details of Method.

Three gm. of the finely powdered root is digested for twenty-four hours with 30 c.c. of benzene. The solution is filtered and transferred to a 200 mm. polarimeter tube, and the rotation is determined in sodium light. The rotenone content is then obtained by multiplying the observed rotation by $\frac{500}{233}$.

Standards.

Derris root contains from 0 to 6 per cent. of rotenone, the average figure being about 2.5 per cent., while the proportion of ether extractive may be up to 20 per cent. Cubé roots, with about the same proportion of extractive, may contain up to 11 per cent. of rotenone, and, owing to the smaller proportion of resins, the extract is lighter in colour and generally crystallises easily.

NITRO-CELLULOSE LACQUERS

PART I.—RAW MATERIALS, MANUFACTURING METHODS, LACQUER FORMULATION.

By W. F. WILSON
Chief Chemist, Messrs. Cellon Ltd.

BEFORE describing the laboratory work on lacquer materials and the finished products, it will be as well to give some account of the components of the modern cellulose lacquer or "dope" and the methods of manufacture.

Nitrocellulose.

Nitrocellulose (or more correctly cellulose nitrate) containing 11-12.5 per cent. nitrogen is still the basis of nearly all lacquers, although many other cellulose derivatives, such as cellulose acetate, ethyl and benzyl cellulose, etc., have been tried. Actually most of the early airplane dopes were made with cellulose acetate, and this ester is still used for certain purposes, but the nitrate is far more important. So far no film-forming material has been produced at an economic price which has all the advantages of nitrocellulose. Although for some purposes cheap lacquers are made containing a very large proportion of cheap resin, such as "ester gum," with only a little nitrocellulose, yet they owe most of their protective properties to this small proportion of nitrocellulose and would be of little use without it.

How Prepared.

The nitrocellulose of commerce is a white fluffy material which is sold damped with about 35 per cent. of ethyl or butyl alcohol. The alcohol renders it safe for transport and handling and is a useful lacquer ingredient. It is prepared usually from purified cotton linters by the action of nitric and sulphuric acids, followed by washing and other treatments. Nitrocellulose is soluble in many organic solvents, and the solutions evaporate quickly leaving a hard tough film of considerable chemical resistivity.

Grades.

It is obtainable in various viscosity grades, i.e., for a solution of given concentration the viscosity may vary from little more than that of water up to a syrupy consistency or even a jelly. The great majority of modern lacquers are applied by spray, and clear lacquers or "varnishes" are often supplied at a suitable spraying viscosity. Pigmented lacquers or "enamels" are usually made rather more viscous to reduce pigment settling, and before spraying must be thinned by 10-50 per cent. of suitable thinners. For most lacquers low viscosity nitrocellulose such as the H.X.45 or half-second type is used. This means that under certain conditions a given steel ball would fall a definite distance through a specified solution of the nitrocellulose in half a second. We shall see later how this important property of viscosity of lacquers is measured in the works laboratory.

It is only in the last few years that stable low-viscosity nitrocelluloses have been produced which can give films which compare in flexibility and durability with those from the high-viscosity "cottons."

PLASTICISERS.

The main disadvantage of a straight nitrocellulose protective film is a tendency to contraction and brittleness when the solvent has practically all evaporated. This difficulty is simply and efficiently overcome by adding a proportion (generally between 10 and 40 per cent. by weight of the dry nitrocellulose) of some substance to render the film flexible without detracting materially from its hardness.

Two Classes of Plasticisers.

Suitable substances may be divided roughly into two classes :—



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Fig. 1.—A PART OF A MODERN LACQUER LABORATORY.

(a) Non-solvent plasticisers or "softeners" such as castor, linseed and other vegetable oils, and

(b) True solvent plasticisers, which are usually ester solvents boiling above 300°C . and practically non-volatile at ordinary temperatures.

The Non-Solvent Plasticisers.

The first class are, of course, much cheaper than the second, and are generally better wetting agents for pigments. However, not being true solvents for nitrocellulose, they are less intimately combined in the film and therefore tend somewhat to "sweat out" at elevated temperatures and to be absorbed from the film when it is applied to very absorbent surfaces.

The Solvent Plasticisers.

The solvent plasticisers are thought to disperse intimately in the interstices of the film and to exert a lubricating effect when the structure is stressed or strained by temperature changes, stretching, impact, bending or vibration. The adhesion and resistance of nitrocellulose films to wear or weathering are greatly improved by correct plasticisation, while the drying rate and hardness are not seriously impaired.

Desirable Properties in a Plasticiser.

The following properties are desirable in a plasticiser—

(1) Miscibility with nitrocellulose, resins and solvents,

(2) Very low vapour pressure so that the plasticising effect is reasonably permanent,

(3) Stability to water, oxidation, light and moderate heat;

(4) Pale colour and freedom from odour;

(5) Wetting power for pigments.

An enormous number of substances, mainly high-boiling esters, have been proposed and tested as plasticisers for nitrocellulose, but most of them are too expensive for general use, even if free from other disadvantages. In this country the three most popular plasticisers are undoubtedly castor oil, dibutyl phthalate and tricresyl phosphate.

Castor Oil.

This is typical in its properties of the non-solvent or "softener" type, but in spite of its disadvantages it is still much used. Leather dopes may contain even as much castor oil as nitrocellulose. The blown oil is widely considered to be superior to the untreated material.

Dibutyl Phthalate, $\text{C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2$.

This is an excellent all-round plasticiser.

If used in conjunction with castor oil the mixture is suitable for pigment grinding and yet has little tendency to sweat out of the film, and thus largely combines the advantages of both substances.

Tricresyl Phosphate ($\text{CH}_3\text{C}_6\text{H}_4\text{O}$)₃PO.

This is equally satisfactory on the whole. It is slightly more permanent than dibutyl phthalate, but has rather more tendency to darken on exposure to light. Like the other ester it is especially valuable in combination with castor oil.

It should be noted that, apart from the true plasticisers, many modern synthetic resins, particularly of the "alkyd" type, confer considerable flexibility on lacquer films containing them, and thus permit reductions in the plasticiser content.

SOLVENT MIXTURES.

Most of the organic liquids which disperse nitrocellulose are comparatively expensive, and lacquer chemists have shown great ingenuity in blending with them cheaper non-solvents or diluents (hydrocarbons and alcohols) to produce moderately priced solvent mixtures. These are chosen so as to evaporate at satisfactory rates to give level-flowing lacquer films without precipitation of any ingredient or of atmospheric moisture ("chilling" or "blushing"). Hundreds of esters, many ketones and some other substances disperse nitrocellulose, but owing to economic considerations only the following true solvents are of outstanding importance in modern British lacquers:—

Ethyl acetate, butyl acetate, amyl acetate, ethyl glycol;
while of less importance are:—

Acetone, ethyl lactate, diacetone alcohol, cyclohexanone and ethyl glycol acetate.

These solvents are produced in enormous quantities in fairly high grades of purity.

Properties of an Ideal Solvent.

The industry has not yet found the ideal solvent, which should have the following properties:—

- (1) Freedom from colour and odour;
- (2) Neutrality and stability;
- (3) High "dilution ratio" (i.e., it should be such a powerful solvent for nitrocellulose that it will tolerate heavy dilution

with cheap hydrocarbon non-solvent). See however (8) below;

(4) Medium evaporation rate to give quick-drying yet good flow-out (a rate similar to that of pure amyl acetate would be suitable);

(5) High solvent power for resins;

(6) It should give dispersions of low viscosity;

(7) It should be non-toxic and non-inflammable;

(8) Moderate price. (If price were sufficiently low, dilution ratio need not be high.)

Ethyl Acetate.

This is a powerful solvent, but its high evaporation rate generally necessitates an admixture of a less volatile solvent. Like the other esters of acetic acid, it has a powerful odour to which, however, the trade has become accustomed under modern working conditions.

Butyl Acetate.

This is made in this country from synthetic *n*-butanol, is to-day the most important lacquer solvent. Its dilution ratio is lower than that of ethyl acetate but higher than that of the amyl ester.

Amyl Acetate.

For many years the premier solvent for lacquers, which were characterised by its "pear-drop" odour, amyl acetate has now yielded place to butyl acetate. The latter is at present slightly cheaper, and less liable to contain small fractions of slowly volatile, strong-smelling constituents.

Ethylene Glycol Monoethyl Ether.

This is usually known as "Cellosolve," and is more expensive than the above esters, but has a high dilution ratio, gives good flow (with slower drying) and has a very mild pleasant odour.

The other solvents mentioned are used only in small proportions (of the order of 5 per cent. of the solvent mixture) to improve flow and prevent "chilling," with the exception of acetone. This liquid is a very powerful solvent, but evaporates far too quickly to be used much in ordinary spraying lacquers, but it is valuable in special quick-drying finishes, adhesives, airplane dopes, etc.

DILUENTS.

Ethanol and Butanol.

Ethanol (as industrial methylated spirit, 64 or 66 o.p.) and Butanol are the important alcoholic diluents. Methylated spirit has a useful solvent action on the "alcohol-soluble" nitrocelluloses of low-nitrogen content, and can be added in large amounts to solutions of the usual ester-soluble "cottons" without causing precipitation. Its mild odour and low price are assets, but unfortunately, large proportions in a solvent mixture tend to cause chilling.

n-Butanol, the usual damping agent for lacquer nitrocellulose, constitutes up to about 10 per cent. of most solvent mixtures because it helps to produce good gloss and flow, to reduce chilling and to blend some resins.

Hydrocarbon Diluents.

These form the major part of most solvent mixtures for economic reasons. Generally the aromatic coal tar derivatives can be added in larger proportions than the petroleum types without causing precipitation, but the latter have milder odours and are lower-priced.

Benzole.

This was for many years an important low-boiling diluent, but is rapidly falling into disfavour on account of its toxicity. Recent Home Office regulations have further reduced its popularity for lacquer use.

Toluole.

This is the most-used diluent, on account of its useful dilution ratio and evaporation rate, and good solvent action on most resins.

Xylol.

This is slightly slower-evaporating and has lower dilution tolerances, but is fairly similar in properties.

Petroleum Diluents.

These on account of their attractive prices, have achieved some popularity in recent years. Fractions boiling between 100° and 150° C. and containing a fair aromatic content are the most suitable. The apparent saving in price produced by using these hydrocarbons is greatly diminished by the fact that their tolerances are less than those of the aromatics,

and therefore, more expensive true solvent must be incorporated.

Arrangement of Solvent Mixture.

Solvent mixtures must always be arranged so that the various components are kept in stable dispersion during storage, and so that the lacquer may be easily applied by the required process (e.g., dip or spray), to dry out to an even homogeneous film. In any nitrocellulose lacquer the slowest evaporating part of the solvent mixture must be compatible with both nitrocellulose and resin, otherwise one component or both may "throw out," giving a whitish irregular film of little decorative or protective value. The only exceptions to this rule are certain fancy finishes which produce a given effect, such as mattness, by the precipitation of one component during the final drying.

Trouble Due to Incorrectly Formulated Solvent Mixtures.

Two troubles sometimes experienced with spraying lacquers are due to incorrectly formulated solvent mixtures. "Chilling" denotes the whitening of the film produced by deposition of atmospheric moisture, and occurs when, owing to the use of too much rapidly evaporating solvent, the air adjacent to the film is chilled below the dew-point. "Orange-peel" is a dimpled effect due to poor flow-out, resulting from uneven evaporation effects. To correct it, the flow-out must be improved by adding a little slowly evaporating solvent such as butanol or ethyl lactate. Both these defects result from the modern tendency to obtain cheaper solvent mixtures and sharper drying by reducing the content of expensive "high-boiler" solvents.

RESINS.

Lacquer technologists have taken advantage of the immense development of modern synthetic resins to incorporate many of them with nitrocellulose; and thereby to enhance greatly the durability and flexibility characteristics of lacquers, while retaining the hardness and quick-setting.

Ester Gum.

However, it should be realised that by far the most important resin for cellulose lacquers is Ester Gum, or rosin ester, which

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Fig. 2.—PART OF A LACQUER MIXING SHOP.
Note the pipeline conveying measured liquids to 500-gallon mixers.

is a modified natural product. When pale rosin is esterified with glycerin, the resulting product is harder, less brittle and of far lower acid value. It is fairly light-fast, very compatible with nitrocellulose, soluble in all the solvents and diluents mentioned except alcohol, and non-reactive with pigments. It imparts good gloss and adhesion to the film, does not cause an inconvenient increase in viscosity, and is always available in consistent quality at a low price. Thus it would be an ideal resin for lacquer work, except that it reduces seriously the durability of nitrocellulose films and has rather poor chemical resistance. It is found in the majority of medium-priced lacquers, either as the only resin or combined with one that is more durable.

Dammar.

This is the most important natural resin used with nitrocellulose. Its pale colour and excellent gloss render it specially suitable for pale wood finishes and whites. Its price is somewhat high, and durability fair. Its solubility is improved by "dewaxing" before use, whereby about 20 per cent. of waxy component

is thrown out from a solution by the addition of methyl or ethyl alcohol.

Among the synthetic resins a great many are compatible with nitrocellulose solutions and can be used to advantage, as explained above; but it is possible to mention only a few types.

Phenolic Resins.

Straight phenol aldehyde resins are not at present popular with lacquer manufacturers, who require a very high standard of light-fastness, i.e., freedom from darkening or yellowing, in their products. Some of these resins display a tendency to incompatibility. The so-called modified phenolic resins are more suitable. A combination of phenolic resin and rosin or ester gum though far less durable than the straight phenolic product, is more soluble and compatible and has better light-fastness. Such a resin gives harder and more durable films than ester gum alone.

Alkyd or Glyptal Resins.

These are proving to be valuable raw materials for the lacquer manufacturer, the straight glycerol-phthalic anhydride

type resins being less useful than the modified derivatives. Pale, flexible, durable resins can be produced not only by modifying the glyceryl-phthalate type with a natural resin (usually rosin), or a plasticiser, but also directly by using dihydric alcohols for the formative reaction. Again, a very large and interesting class of resins results from the modification of glyptals by drying-oils, e.g., linseed oil, and their acids. These are darker in colour than the other types, but are still compatible with nitrocellulose and give valuable combination lacquers. They are superior to the drying oils themselves for this type of finish on account of their greater hardness and more rapid setting. Many of the well-known Rezyl, Beckosol and Paralac resins belong to this class.

With the aid of the latest glyptal resins lacquer manufacturers can produce quick-drying finishes of a standard of pale colour, durability and flexibility never attained before; and when suitably pigmented these finishes can give "enamels" of great purity of colour and permanence.

PIGMENTS.

Pigments for cellulose lacquers must fulfil requirements which are very different from those specified for oil paints and enamels. In the latter case more emphasis is laid on moderate price, while if possible the pigments should aid the drying process of the medium and perhaps even react mildly with it. Oil media have a relatively higher non-volatile content than lacquers and thus permit the use of greater pigment concentrations without the risk of undue mattness or tendency to cracking.

Lacquer media, however, rarely contain more than 1½-2 lb. per gallon of non-volatiles at spraying consistency and the films are comparatively thin. Only low concentrations of pigment are allowable and thus pigments for cellulose must be of maximum strength, fineness and opacity. They should preferably be easily dispersed, as some cellulose media are far from being ideal for grinding purposes, yet superlatively fine dispersion is necessary for good lacquers. Cheap extenders, which are widely used in oil finishes, are almost unknown, as such, in lacquers. Much use is made of strong, bright lakes and pigment dyestuffs, but these should be as far as

possible insoluble ("non-bleeding") in the powerful lacquer solvent mixtures.

Owing largely to the low acidity of most lacquers, "livering" or "feeding" troubles are comparatively rare. On the other hand, some pigments which are satisfactory in paints are unsuitable in various ways for lacquers; for example, some Prussian blues display objectionable bronze undertones in lacquers. Pigments for high-class exterior lacquers such as automobile finishes must have maximum fastness to light. Cellulose media are generally very pale, and to meet the requirements of many "luxury" industries the brightest and purest colours are necessary. From the large number of pigments used the following are probably the most important.

White Pigments.

Titanium White is the most suitable white on account of its exceptionally high opacity and strength. A suitable grade for lacquers contains 40-50 per cent. TiO_2 and 60-50 per cent. blanc fixe (precipitated barium sulphate). The pure titanium dioxide is less used. Titanium white is chemically inert; but is often mixed with other whites for outside use on account of its objectionable tendency to "chalk" excessively.

Antimony White ("Timonox") is also widely used, but is inferior to titanium white in strength, opacity and whiteness, although softer and less prone to chalk.

Zinc Oxide gives an excellent white and is perhaps the most easily dispersed, but although cheaper than titanium it is inferior in opacity and strength. "White seal" oxide is of very high chemical purity.

Lithopone is a very good cheap white, especially for interior work. The usual grade containing 30 per cent. ZnS , 70 per cent. blanc fixe has better hiding power than zinc oxide, but is less stable chemically.

Black Pigments.

Carbon Black, made from natural gas, is very suitable for lacquers because of its great strength, opacity and permanence. The most intensely coloured grades are preferred, although often very difficult to disperse.

Bone Black and *Vegetable Black* are both far inferior in strength, and are used mainly for pale tints.

Black Lakes, frequently from logwood, are used occasionally where maximum intensity of colour is required at some sacrifice of light-fastness.

Reds, etc.

Oxide Reds.—The artificial iron oxide colours are generally more suitable than those occurring naturally, as they are brighter and stronger. They are available in a wide range of shades, from yellow to purple.

Toners and Lakes.—More important for most lacquer purposes because of their brilliance are the organic reds. They may be either the pure insoluble pigment dyestuff or a strong lake formed by "striking" a dyestuff on a suitable substratum such as blanc fixe.

Lithol Red and *Helio Fast Red* are popular colours, sometimes employed as pure toners.

Alizarine Red, though duller and more transparent, is valued for its permanence.

Among the purple and maroon colours used in lacquers we may mention the lithol rubines and the newer "Fanal" lakes derived from basic dyestuffs such as magenta by the action of complex inorganic acids.

Cadmium Red, although its permanence is an advantage in pale pinks, is rarely used on account of its high price coupled with poor staining power.

Yellows.

Natural *Ochres* are too weak and transparent for lacquer use, but the artificial yellow oxides ("ferrite yellows") are employed.

Chromes.—*Zinc Chrome* gives a bright useful primrose, stable to sulphur fumes. Neutral and basic lead chromates give rise to the valuable *Lemon*, *Middle*, *Orange* and *Scarlet* Chromes which are strong and inexpensive.

Cadmium Yellows based on cadmium sulphide are becoming more popular for lacquers, in spite of their high price, because of their fastness to light and sulphur fumes.

Browns are largely obtained by tinting but *Burnt Umber* is a cheap and useful brown, although rather coarse by lacquer standards.

Blues.

Ultramarine, a complex of sodium

aluminium silicate, sodium sulphide and sulphur, is the cheapest blue, and though rather weak and transparent is very useful for reddish tints. It has good fastness to light and alkali.

Prussian, Chinese and Non-bronze Blues, all essentially ferric ferrocyanide, are strong colours of rather poor hiding power which yield excellent greenish-blues and greens. For lacquers the least "bronzy" types are preferred, in spite of their notoriously difficult grinding properties. These blues are very sensitive to alkali.

Blue Lakes are used occasionally for the brightest shades, but the usual grades are of rather poor light-fastness.

Greens.

A large range of greens can be made by mixing chromes and Prussian blue, but the manufactured "wet-struck" *Chrome Greens* are preferable. They are strong pigments of good opacity and moderate price.

Chromium Oxide and *Guignel's Green* are weak but very permanent pigments.

For very bright shades, *Green Lakes* are used, usually either of the "Fanal" type or Naphthol Greens.

Metal Powders.

Many pleasing finishes of good durability are obtained in shop-front and theatre decoration, as well as on small articles, by the use of bronze powders stirred into suitable clear nitrocellulose bronzing media. Aluminium powder is particularly popular for aircraft dopes and lacquers.

Lacquer-soluble Dyes.

These are sometimes used, alone or together, with pigments to obtain particularly intense or bright colour effects and to improve hiding power without reducing the gloss of the film. The yellows, oranges and browns are probably the fastest to light, but the blacks are the most important. Nigrosine or its resinate, etc., are often added to lacquers pigmented with carbon blacks to improve the intensity of the colour, and the combination has good fastness and hiding power, although the film is liable to "bleed" if a light colour or clear lacquer are applied later.

MANUFACTURING PROCESSES.

It will be advisable to give a brief

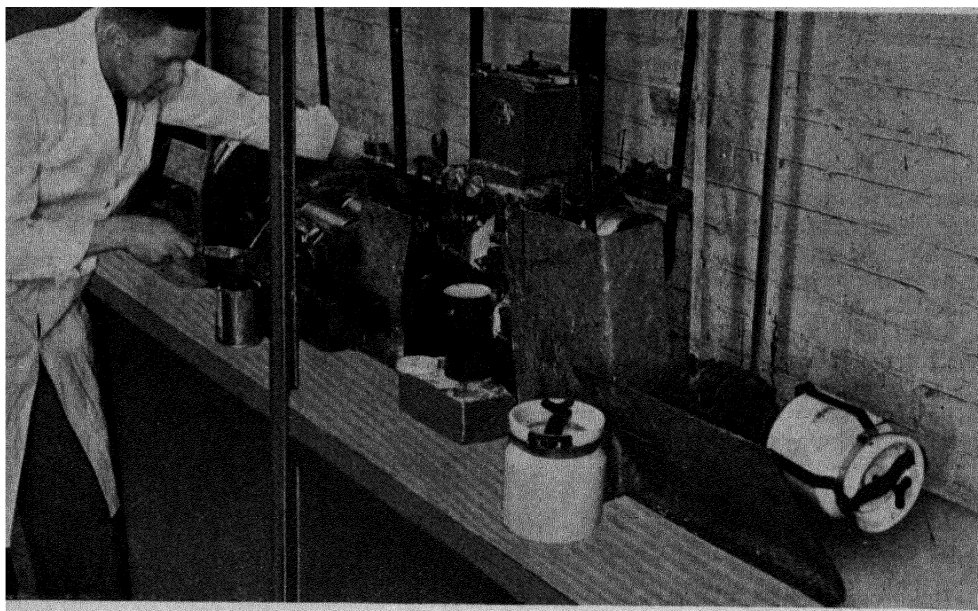


Fig 3 —PART OF A LABORATORY MILL BENCH
A pigment-plasticiser paste is being ground on a triple roller mill

description of the methods of lacquer manufacture and to show how the works chemist guides and controls the processes, while his research colleague develops new products and improves existing ones.

Storage of Raw Materials.

Nitrocellulose is a highly inflammable material even when damped with butanol. It is supplied in air-tight galvanised drums containing approximately 120-170 lb. These should be kept in a separate building with a wooden or composition floor. The store should be kept locked and should have no artificial lighting or heating. Nitrocellulose should never be allowed to become dry as in this state it is readily ignited by sparks, heat, etc.

Solvents.

The main solvents and diluents are supplied either in 50-100 gallon drums or in bulk and in a large factory are stored in underground tanks, from which they are blown through suitable pipes to the mixing shops. The solvent store should be well-ventilated and the lights and switches should be of the "dangerous atmosphere" type.

Plasticisers, Resins and Pigments.

These can be stored without restrictions.

It is important that the pigments should be kept in a dry place as some are very hygroscopic.

Mixing Plant.

It is advisable to stock a few concentrated solutions of nitrocellulose for use in small runnings, and when maximum clarity of solution is required. However, for the usual large batches the nitrocellulose is dissolved with the other ingredients as required. The resins, particularly those brought in lump form, such as ester gum, dammar, etc., are best dissolved separately in churns containing a few balls or in mixers, to give resin base mixtures of about 50 per cent. concentration. For these, typical solvent mixtures are used, so that when the resin solutions are added to the other ingredients no local precipitation of nitrocellulose occurs, as would happen if the resin were cut in straight hydrocarbons. The resin solutions may be readily clarified, owing to their low viscosity, by filtration, centrifuge or simply settling. The main mixers may be of 100-500 gallon capacity and of the vertical cylindrical type, made of galvanised iron and with close-fitting lids. They are fitted with stirrers, baffle-plates and discharging gauge-taps.

Making a Typical Clear Wood Lacquer.

The procedure for making 500 gallons of a typical clear wood lacquer would be as follows:—

First, a part of the non-solvents or diluents, including all the alcoholic constituents, are blown over into the mixer from the solvent store tanks via the measuring apparatus. The nitrocellulose is added and allowed to moisten thoroughly. Then the plasticisers and resin solution and all the solvents are added and the mixer run until the nitrocellulose is dispersed. Finally the remaining diluent is added with the mixer running to prevent local precipitation. By initial wetting-out of the nitrocellulose by non-solvent the true solvents are helped to strike through the mass of cotton and the formation of masses of gel is reduced as far as possible. In this way dispersion is most speedily effected.

Pigment Dispersion.

Pigments for lacquers must be very finely dispersed because, as previously explained, lacquer films are very thin and only a small concentration of pigment can be used. Further, lacquer solvents are fairly expensive and highly volatile compared to paint thinners, and the vapours are highly inflammable. Therefore whenever pigments are ground in media containing cellulose solvents the plant must be carefully enclosed. This means firstly that cone or flat stone mills are relatively unsuitable, as their slow action, together with the rapid drying of the lacquer, cause evaporation losses and even accumulation of semi-dry lacquer at the scrapers. Secondly, when pigments are ground on triple-roll mills, the medium must not contain any considerable amount of volatile liquid, as it is impracticable to enclose these mills and prevent evaporation.

Using a Ball-mill.

In practice there are two main methods of pigment dispersion. By the first method the complete lacquer components (with the possible exception of part of the solvent mixture) are placed in a ball-mill of 10-100 gallons capacity, and the mill is run until the pigment is thoroughly dispersed in the medium. The lacquer is then transferred, preferably by gravity or compressed air, to a single-roller refining mill, which is enclosed to prevent evaporation, and which removes any coarse

particles or impurities, giving a high-grade lacquer or enamel ready for packing. The ball-mills are preferably lined with porcelain or silex, and are charged with pebbles which grind the pigment by combined impact, shearing and mixing as the mill rotates. Ball-mills are slow in action and difficult to clean, but have the following advantages:—

- (1) Reasonable cost, and low upkeep and power consumption.
- (2) Fine grinding.
- (3) No volatile loss.
- (4) No attention is needed while grinding.

They are best suited to repetition batches of the same colour. The single-roller refining mills can be well enclosed and have a high output. They have little actual grinding action.

Using a Triple or Quadruple Roller Mill.

The alternative method of grinding is on the triple or quadruple roller mill. The pigment is kneaded and mixed with the plasticisers in a knife mixer or "pug" until partially wetted. It is then transferred to the roller mill. These mills have three or four steel or granite rollers, often water-cooled, which are geared so as to rotate at different speeds, one roll often having a lateral motion as well. The pressure between the rolls is adjustable, and a powerful shearing action is exerted by the differential speeds. These mills grind well and have a high output, while they are easily cleaned. However, their initial cost is high.

Whereas, by the ball-mill method the pigment is ground in the complete lacquer, the plasticiser pigment paste obtained from the roller mill needs to be incorporated in a clear lacquer by a high-speed mixer, the whole being then usually refined.

A very high standard of dispersion is attained in good quality lacquers made by either process.

IMPORTANT TYPES OF LACQUERS AND DOPES.

We have now described the more important lacquer ingredients, and outlined the mixing and grinding processes by which the lacquers are produced. It will be noticed that lacquer manufacture is conducted throughout at ordinary temperature and does not entail, as in varnish

making, troublesome heat-treatment of raw materials and products, or long maturing. However, rigid scientific control must be exercised.

We will now describe briefly some of the types of nitrocellulose finishes which have won a firm position in the industrial world owing to their outstanding advantages over older finishes.

Metal Lacquers.

These are used to protect bright metal surfaces, and in some cases to enhance the gloss. They must give thin, hard durable

films, which are acid-free and unblemished by specks or cloudiness and which have great adhesion to various metals. Many such lacquers contain little or no resin so as to obtain maximum paleness. Medium-viscosity nitrocellulose is often preferred as giving less brittle films than the low-viscosity types, and an adequate amount of light-fast plasticiser is

added to enhance the adhesion. If resin is used, a small proportion of dammar or glyptal is suitable

Automobile Lacquers.

Most motor-cars are finished in cellulose lacquer which is far better suited to modern mass-production than coach-painting methods. Also the finish offers great resistance to tar, oil, petrol and abrasion. In modern practice low-bake synthetic resin primers are preferred because of their great flexibility and adhesion. The finishing cellulose lacquer is formulated for maximum durability and colour retention, and gives a hard finish which easily takes a high polish. A high solid content and low resin/nitrocellulose ratio are customary,

the resin being a glyptal or dammar. Ester gum is not advisable in durable lacquers of this type. The black lacquers are often intensified in colour by the addition of dye.

Aircraft Dopes and Lacquers.

Large quantities of "dopes" are used on the fabric wings and fuselages of airplanes and the envelopes of airships in order to tauten, strengthen and waterproof them. Formerly these were largely made on a cellulose acetate basis, on the ground of alleged lower inflammability, but the

nitrocellulose dopes are more general to-day. Dope films must not crack on exposure, but on the other hand the plasticiser is carefully chosen and limited so that the fabric is firmly tautened on the wings or framework. Many other parts of aircraft besides wings, etc., are finished in cellulose lacquer.

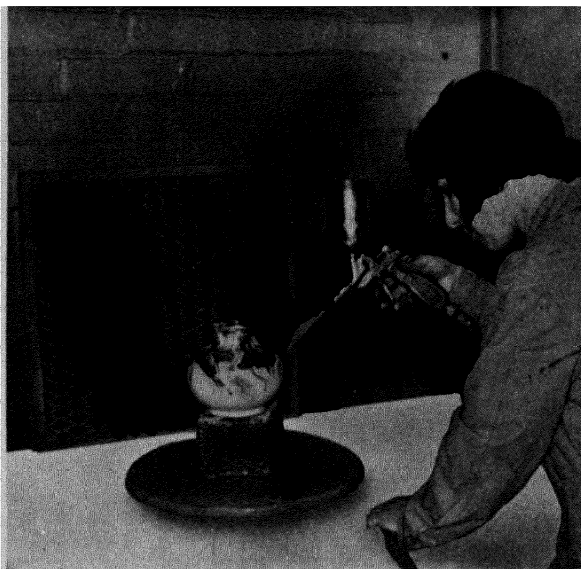


Fig. 4.—SPRAYING POTTERY LACQUER

The spraying is conducted in a booth, behind the grating is a 2 ft fan

Industrial Lacquers.

Although the use of cellulose

is not extensive in the heavy industries such as engineering and shipbuilding, lacquers find innumerable applications in industry whenever very cheap full-bodied finishes are not required. Radio cabinets, toilet goods, toys, countless fancy goods in the "luxury" trades, pencils, leather, artificial leather and fabric articles, handles, physical and chemical apparatus, are a few examples, and it will be seen that a very varied range of lacquers is included in this class.

Furniture Finishes.

These, both transparent and pigmented, form one of the most important groups of lacquers. All kinds of furniture are treated and the lacquer finish is superior

to french polish in ease of application, durability and suitability for modern decorative schemes. The types of finish range from full-gloss through satin and velvet to matt.

APPLICATION METHODS.

For most purposes lacquers are applied by spray, although for many purposes dipping, brushing, tumbling or roller methods are used.

Spraying.

Great progress has been made in the last ten years in the manufacture of lacquer spraying plant, and spraying is the rational and economical method for lacquering large surfaces and medium-sized articles evenly and thoroughly. Compressed air at 20-80 lb./sq. in. is used; the spray-guns have a variety of jets, they can be adjusted to give flat or round sprays, and they are as readily cleaned as a brush. For mass production work the guns are fed from lacquer tanks provided with bubble or stirrer agitation. In fact, in many factories automatic spraying plant is installed. Wherever spraying is practised, proper cabinets with efficient ventilation must be provided to remove the large amounts of evaporated solvent. The spray-shop should be maintained at 60-70° C. with only moderate humidity to obviate "chilling."

Drying.

Forced drying in low temperature ovens is common, e.g. in the motor industry; although not essential for the drying process, by accelerating evaporation of the solvent it enables the film to reach quickly its maximum hardness. For cellulose use the ovens must be heated only by steam or electricity and must be well ventilated. For most purposes a drying period of $\frac{1}{2}$ -1 hour at 50-70° C. would be satisfactory.

Clear lacquers intended for spraying are often supplied at a viscosity suitable for the purpose, say 1 to 2 poises or less. However, many users prefer to receive their lacquers at a higher viscosity, so that they may thin as required for various jobs.

Pigmented lacquers, to avoid pigment settling, are almost invariably sent out in a fairly viscous form. In a lacquer high viscosity does not of course necessarily

imply high solid content. A lacquer having a viscosity of 10 poises might be made with a nitrocellulose content of only 5 per cent.; while another could be made with 15 per cent. of a low viscosity nitro-cotton to give a considerably lower viscosity. The average spray lacquer is thinned perhaps 25 to 50 per cent., depending on the surface to be sprayed, the air pressure, size of spray-gun jet and the nature of the lacquer. Many lacquers, for example some leather dopes, and first coats on porous surfaces generally, are thinned up to 200 per cent.

Dipping.

This is a simple method of application which can be well adapted to lacquering many articles, from bicycle frames down to pencils, spools, handles, etc. A successful finish is best obtained by simple automatic dipping machines, which dip and withdraw the articles so slowly (about 1 to 4 cm. per minute) that an even coating is applied free from "runs" and "tears." Very small, mass-produced articles may be dipped in a wire cage, followed by draining, shaking and forced drying; or they may be "tumbled" in a drum containing just sufficient lacquer.

Brushing Lacquers.

Although serious attempts were made to produce brushing lacquers for architectural decoration, it must be admitted that they met with little success. It was necessary to use only low-viscosity lacquers to permit brushing at all on large surfaces and even with the slowest-evaporating solvents (which incidentally are the most expensive) the lacquer films set so quickly that they soon dragged under the brush and rendered it very difficult to obtain a level film. The films produced were very thin compared to those given by enamel paints, and successive coats tended to "pick up" the first coat, which even when hard remained soluble in the lacquer solvents. However, a considerable amount of cellulose lacquer is still applied by brush on small surfaces, largely through the "household tin" trade.

FORMULATION.

Considering that all the manufacturing operations are conducted at atmospheric temperature, without any blending or "bodying" under heat, as in the varnish

industry, a surprisingly wide range of lacquer products can be produced using the raw materials previously described. A few points in connection with the preparation of lacquer formulæ may be of interest.

Units.

The chemist will obviously work in the usual C.G.S. system of units used in every laboratory, grammes and c.c.s. This is particularly necessary when dealing with plasticisers of which only small amounts are used. These are usually converted to pounds and gallons for work practice, although the metric system is employed in a few factories.

Apparatus Required.

The apparatus for formulation work will be very simple. A rough balance, weighing up to 1 kilogramme to within 0.1 gm., and an analytical balance for solid content determinations and small weights, will be required. For measuring solvents, 10, 25 and 100 c.c. measuring cylinders and 5 or 10 c.c. graduated pipettes are suitable. The more important solvents and plasticisers can conveniently be kept in bottles with burettes fitted. For preparing nitrocellulose and resin solutions, 8 and 16 oz. bottles which can be fitted into a mechanical shaking device are useful. An electrical geared stirrer is a great convenience, especially if provided with assorted paddles for fitting in a chuck. The commoner resins can be kept in 1-pint lever-lid tins, and the bulkier nitrocellulose in 1-gallon tins, the obvious precautions being taken against sparking and proximity to lights.

How Fine Dispersion is Obtained in the Laboratory.

Pigment dispersion is a serious problem for the small laboratory. For accurate work fine dispersion is essential. The simplest possible contrivance—ignoring the homely muller or pestle and mortar—is a ball mill arranged from a tin containing large ball-bearings and rotated by an electric motor. Needless to say, superfine grinding cannot be expected from it.

The ideal equipment is a mill bench fitted with 6-in. triple roller mill, and laboratory ball- and single-roller mills, all driven by a $\frac{1}{2}$ h.p. motor. Only in this way can works production be anticipated

on the small scale, and such an outfit is invaluable in trying out new raw materials and investigating works problems. However the initial outlay represents a very heavy item in laboratory expenditure, even in these enlightened days.

Thinning Out Pigment Pastes.

For thinning out pigment pastes a miniature mixer is unnecessary. A spatula with a thin 6-in. blade and an evaporating basin or a bell-shaped measure are quite suitable. Incidentally these measures are ideal for blending quantities of lacquers up to 1 pint, above which the familiar enamelled quart measure may be employed. Measuring cylinders are unsuitable for handling lacquers owing to the viscosity of these products. Among the other desiderata may be mentioned glass and metal slides for tests, and a supply of small tin containers. We assume that the usual laboratory equipment will also be available. Actually many other items of apparatus are constantly used, some of which are better considered under the heading of Raw Material and Lacquer Testing.

A Process of Formulation.

It is suggested that the formulation of a lacquer may proceed in four steps:—

- (1) Determination of desired properties.
- (2) Selection of non-volatile ingredients.
- (3) Selection of volatile ingredients.
- (4) Adjustments and improvements.

(1) For the experienced technologist this will be a matter for perhaps two or three minutes' thought, to decide just how he can compromise between the various properties of gloss, hardness, flexibility, drying rate, durability, odour, covering power, colour, adhesion and, often above all, cost.

(2) In deciding on this, the "business" part of the formula, the chemist may first settle on his solid content, resin/nitrocellulose, plasticiser/nitrocellulose, and viscosity figures, which are largely interdependent. Then he can write down the quantities of non-volatiles, nitrocellulose, resin, plasticiser and pigment necessary for 100 gallons of lacquer.

(3) He will then choose a solvent mixture suitable for dispersing the solids and, having estimated the bulking value of the latter, will draw up his quantities of solvents.

(4) Finally, having tested his provisional formula, any necessary adjustments can be made to conform with the specification drawn up in section (1).

A Formula for a Clear Wood Lacquer.

As an example, we may desire a formula for a moderate-priced clear wood lacquer for interior use. Good gloss and high body are required. A solid content of 3 lb. in a gallon and a resin/nitrocellulose ratio of 2.3 are suggested. A fairly low viscosity nitrocellulose must be used, but the resin may be as dictated by considerations of cost, colour, toughness, or the preference of the formulator. The plasticiser may be 20 per cent. of tricresyl phosphate, calculated on the dry nitrocellulose. Then for 100 gls. we have as "non-volatiles" :—

H.L.30 nitrocellulose or		Approximate
4 sec. type damped with		bulking
35 per cent. butanol ..	132 lb.	value.
Pale ester gum ..	132 "	11 gls.
Dewaxed dammar ..	66 "	18 "
Tricresyl phosphate ..	17 "	1½ "
Total		<u>30½ gls.</u>

We then require 69½ gls. of a suitable solvent mixture to give a clear solution which dries quickly and levels well to a hard glossy film.

The Final Formula.

The final formula might well be :—

Damp H.L.30 nitrocellulose or	
4 sec. type	132 lb.
Pale ester gum	132 "
Dewaxed dammar	66 "
Tricresyl phosphate	17 "
Butyl acetate	9½ gls.
Ethyl acetate	10 "
Butanol	3½ "
64 o.p. spirit	3½ "
Toluole	36 "
Xylol	7 "
Total	<u>100 gls.</u>

The Spraying Thinner.

A suitable spraying thinner for the

above or many other lacquers would be :—

Butyl acetate	21 gls.
Ethyl acetate	12 "
64 o.p. spirit	7 "
Toluole	50 "
Xylol	10 "
Total	<u>100 gls.</u>

Formula for a High-class Automobile Lacquer.

An example of a high-class modern automobile lacquer would be :—

Damp H.X. 45 nitrocellulose or	
½ sec. type	250 lb.
Rosin-modified glyptal	67 "
Diamyl phthalate	30 "
Tricresyl phosphate	30 "
Butyl propionate	3 gls.
Butyl acetate	12 "
Ethyl acetate	7½ "
Butanol	4 "
Toluole	26 "
Xylol	10 "
64 o.p. spirit	5 "
Pigment paste ground in blown	
castor oil	125 lb.
Total	<u>104 gls.</u>

Formula for a Cellulose Bronzing Medium.

A typical cellulose bronzing medium might have the formula :—

Damp H.L. 130 nitrocellulose or	
15-20 sec. type	75 lb.
Ester gum	20 "
Dibutyl phthalate	10 "
Butyl acetate	12 gls.
Ethyl acetate	16 "
Butanol	5 "
64 o.p. spirit	8 "
Toluole	42 "
Xylol	8 "
Total	<u>100 gls.</u>

For successful formulation it is essential that all raw materials be of consistent good quality, and regular routine tests should be made in every batch to ensure this. A later article deals with routine tests and analyses.

THE INDIA RUBBER INDUSTRY

PART I.—THE MANUFACTURING PROCESSES

By J. R. SCOTT, Ph.D., F.I.C.,

Research Association of British Rubber Manufacturers

Source of Rubber.

THE material variously known as "rubber," "india rubber," or "caoutchouc" is of vegetable origin, being found in numerous plants growing in tropical and sub-tropical countries. Of these plants the most important commercially is *Hevea Brasiliensis*, a tree indigenous to the Amazon valley, but now cultivated on a vast scale in the rubber plantations of British Malaya, the Dutch East Indies, Ceylon, India and neighbouring countries. These plantations are to-day the chief source of rubber, and produce over 800,000 tons yearly. The trees growing wild in the tropical Amazonian forests were at one time the main source of rubber, but then output (about 10,000 tons a year) is now relatively insignificant.

Latex.

The rubber in *Hevea Brasiliensis*, as in most rubber-yielding plants, occurs in the form of a milky juice called

"latex," which consists of minute rubber particles ($\frac{1}{10000}$ of an inch or less in diameter) suspended in a watery liquid or "serum," in much the same way that the particles of butter fat are suspended in milk. Latex normally contains 30 to 40 per cent. of rubber. To extract the latex from the tree a cut is made in the bark, the latex then slowly trickles out and is collected in a cup.

Preparation of Crude Rubber.

The rubber must now be separated from the latex; this is done by one of two general methods, namely, by drying off the watery "serum" and leaving the solid rubber, or by coagulating or curdling the latex by adding an acid.

The drying method has been used for centuries by the natives of the Amazon valley. The blade of a wooden paddle is dipped into the latex and held in the smoke from a wood fire till



Fig 1.—COOLIE TAPPING A RUBBER TREE
A slanting cut is made through the bark, when the latex slowly oozes out and trickles down into the cup affixed below the tapping cut

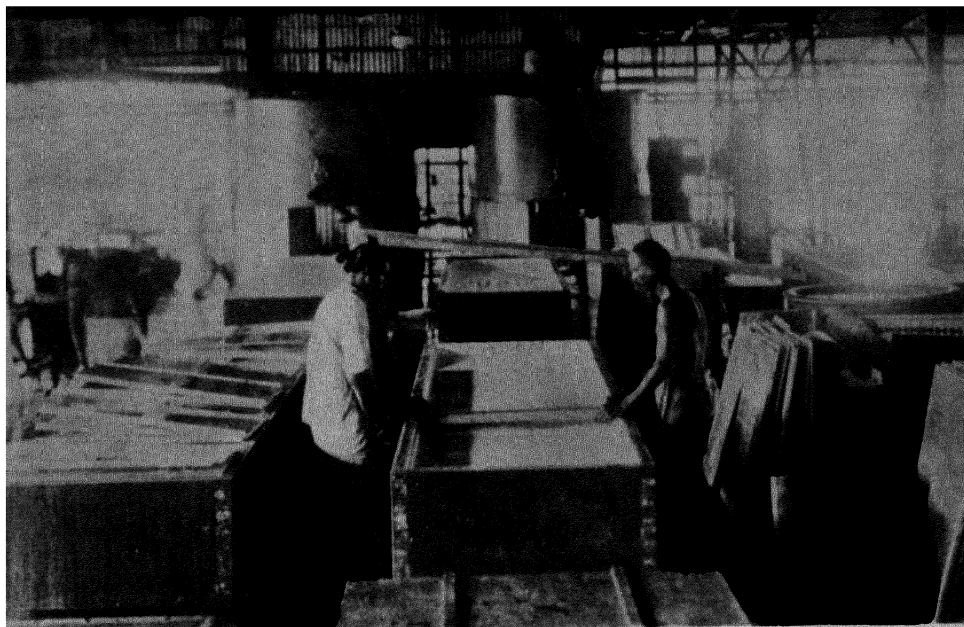


Fig. 2.—COAGULATING TANKS.

The rubber latex is coagulated in these tanks by adding an acid. The tank is divided by vertical partitions into narrow sections, in each of which a slab of the coagulated rubber or "coagulum" is formed, suitable for rolling out into "crêpe" or "sheet."

the latex film is dried. By repeating this process a large ball of rubber is gradually built up on the paddle. The product is known as "Para" rubber, after the town of Para or Belem, from which much of it is exported.

The coagulation method is that used universally on the rubber plantations in the East. The latex from the thousands of trees on the estate is bulked in large tanks, diluted to a standard rubber content, and coagulated by adding a little acetic or formic acid. The latex sets to a junket-like mass from which the serum gradually separates, leaving a soft spongy clot or "coagulum" of rubber, which is then treated by one of two methods. In one method the "coagulum" is passed between rollers which squeeze out most of the remaining serum and is then dried in smoke-laden air from a wood fire. This produces the "smoked sheet," or "ribbed smoked sheet" of commerce, in the form of brown translucent sheets about $\frac{1}{8}$ in. thick. In the other method, the coagulum is torn to shreds and thoroughly washed between grooved rollers under a jet of water, then rolled out

into thin sheets and hung up to dry in well-ventilated sheds. This gives the rubber known as "pale crêpe," in the form of thin, rough, yellowish-white sheets. The familiar crêpe rubber soles are simply a specially thick form of this kind of rubber. In order to obtain a very light-coloured crêpe, for which there is a demand, sodium bisulphite is often added to the latex as a bleaching agent.

The rubber, in the form of smoked sheet or crêpe, is packed in wooden cases holding about 160 to 200 lbs., and shipped in this form to the manufacturing countries of Europe, America and elsewhere.

In recent years the development of processes for the manufacture of rubber articles directly from latex has led to the exporting of large quantities of latex in liquid form, after the addition of a preservative such as ammonia; sometimes, also, the latex is concentrated to avoid having to transport so much useless water.

The material we have so far designated as "rubber" is more precisely termed "raw" or "crude" rubber, since it is the basic raw material in the manufacture of rubber goods.

Properties of Raw Rubber.

Raw rubber is a tough gristly material consisting essentially of the substance "caoutchouc," together with small amounts of fatty acids, resinous substances, sugars, protein and mineral matter. Caoutchouc is a highly polymerised unsaturated hydrocarbon of the formula $(C_5H_8)_x$, believed to consist of long chain-like molecules formed by the linking together of a great many molecules of isoprene (C_5H_8) .

Rubber in its raw or crude state would be quite unsuitable for the vast majority of the articles at present made from rubber. Thus, it is too sensitive to changes in temperature, for it becomes quite hard and stiff in the cold, but soft, flabby, and even sticky when hot. It is attacked by liquids like petrol, benzene, paraffin, and lubricating oil, which cause it to swell to a sticky mass and ultimately dissolve. Its elastic properties are very far from satisfactory, for it does not recover anything like completely after being stretched or compressed. Finally, raw rubber is all very much alike, whereas the manifold uses of rubber goods demand a wide range of variation in such properties as colour, extensibility, hardness, and resilience or elasticity (con-

sider, for instance, the difference between catapult elastic, a brightly coloured hot-water bottle, the tough "tread" of a motor tyre, a soft crumbly eraser, and the extremely hard leather-like black rubber used for soles and heels). For these reasons the properties of raw rubber must be modified so as to remove its shortcomings and to make possible the wide range of properties demanded in the finished products. These modifications are brought about by the processes of "vulcanisation" and "compounding."



Fig 3—INTERIOR OF A "SMOKE HOUSE"
Showing the sheets of rubber hung up to dry in the hot, smoky air provided by a wood fire.

Vulcanisation.

Two general methods of vulcanisation are in use. The most widely used is "hot" or "sulphur" vulcanisation, in which the rubber is mixed with sulphur and heated. Normally the amount of sulphur is only 2 to 5 per cent. of the rubber, but if it is increased to 35 to 50 per cent., the product known as "hard rubber," "ebonite," or "vulcanite" is obtained. In the

other method, known as "cold vulcanisation" or "cold curing," the rubber is treated with sulphur monochloride (S_2Cl_2) without heating. For this purpose the rubber is either dipped into a dilute solution of sulphur monochloride in carbon disul-

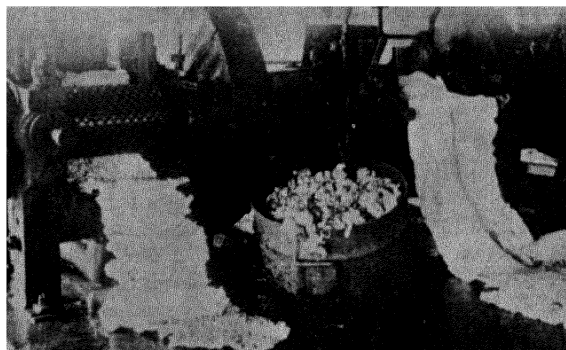


Fig 4—CRÊPEING MACHINES, ON WHICH THE "COAGULUM" IS ROLLED OUT, BY PASSAGE BETWEEN IRON ROLLERS, INTO THE THIN ROUGH SHEETS WHICH, AFTER DRYING, FORM "CRÊPE" RUBBER

phide or carbon tetrachloride, or else exposed to the vapour of sulphur monochloride. As the sulphur monochloride has to penetrate into the rubber from the outside, these methods can obviously only be used for thin-walled articles like toy balloons, rubber gloves, etc., or for the thin layers of rubber applied to waterproof (macintosh) fabrics.

Compounding.

The term "compounding" denotes the incorporation into the rubber of materials which give to the finished product the particular properties desired, or which facilitate the processing and handling of the rubber during manufacture. Those unfamiliar with rubber technology are apt to assume that such additions are merely adulterations which cheapen and lower the quality of the product. This is very far from the truth, for many of the added materials are more expensive than rubber itself, and without the use of these materials or "compounding ingredients" many of the present-day uses of rubber would never have been possible.

Compounding ingredients can be classified into: (i) Pigments, added to give the de-

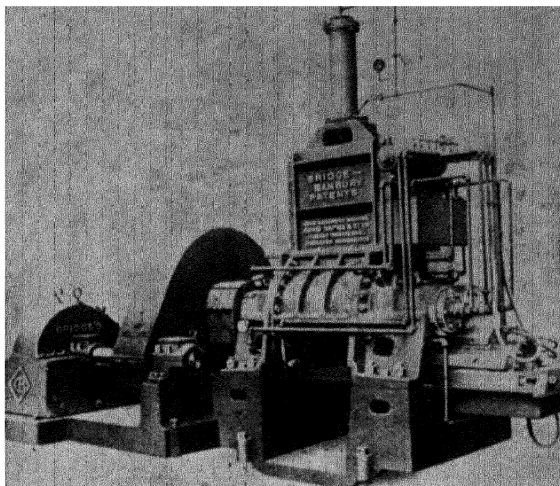


Fig. 5.—AN "INTERNAL MIXER," THE LATEST TYPE OF MACHINE USED FOR MIXING RUBBER "STOCKS."

Machines of this type will mix anything up to half a ton of "stock" at once.

sired colour; the mineral pigments originally used are now largely displaced by synthetic coal-tar colours. (ii) Fillers, added to stiffen and harden the rubber when strength and wear-resistance are not important (examples: whitening, ground barytes, powdered talc, kieselguhr, and coarse clays). (iii) Reinforcing agents, which give greatly increased strength, toughness and resistance to wear (examples: zinc oxide, colloidal china clay, litharge, basic magnesium carbonate, and above all "gas black," a form of carbon made by burning natural gas). (iv) Softeners, i.e., oily or waxy substances added to prevent the rubber becoming too stiff by the admixture of dry powders. (v) Accelerators, complex organic substances which speed up the process of hot vulcanisation with sulphur. (vi) Antioxidants or antioxygens,

used to retard the oxidation of rubber by atmospheric oxygen, which is the chief cause of the gradual deterioration or perishing familiar to all users of rubber goods.

Two other constituents extensively used in rubber goods must be mentioned; these are "rubber substitute" or "factice,"

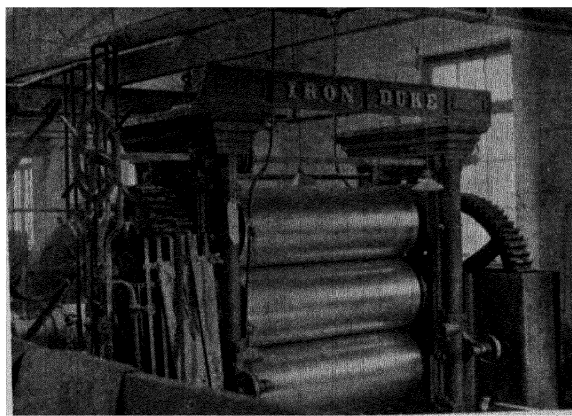


Fig. 6.—A RUBBER "CALENDER."

Showing the polished steel rolls used for sheeting out the plastic rubber "stock" or for "frictioning" it on to fabrics.

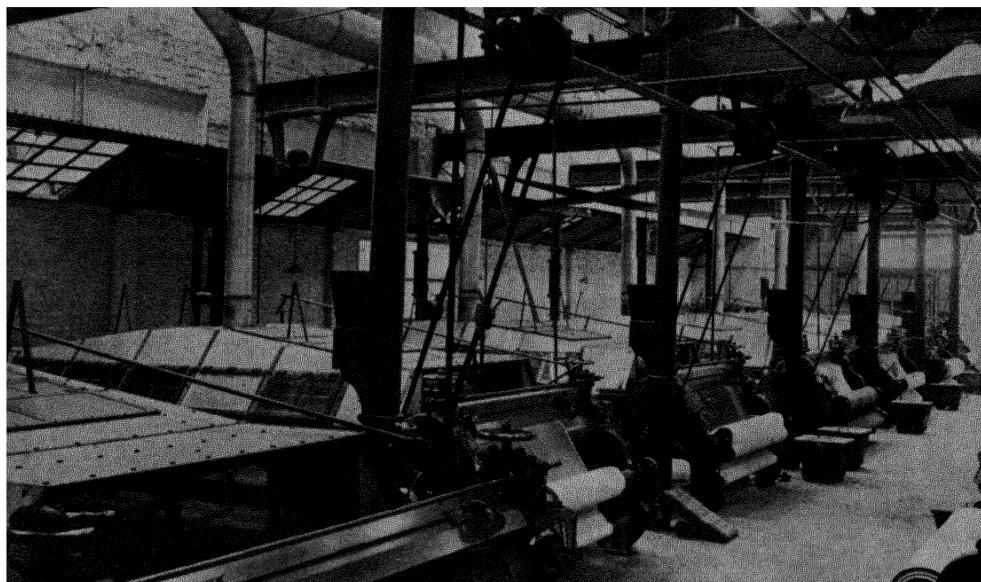


Fig 7 —A BATTERY OF "SPREADING MACHINES," USED FOR COATING FABRICS WITH A THIN LAYER OF PASTY RUBBER "DOUGH"

The drying tables at the rear of the machines are enclosed in hoods for the purpose of recovering the vapours of the solvent evaporated from the coated fabric

made by the action of sulphur or sulphur monochloride or vegetable oils and used mainly in erasers and waterproof fabrics, and "reclaimed rubber" or "reclaim," made by heating and plasticising old waste vulcanised rubber and used as a partial substitute for new raw rubber

Chemistry has played an important part in the development of the science of "compounding." The coal-tar dyes which have made possible the gaily coloured bathing caps, toys, hot-water bottles, rubber aprons, etc., of to-day, the organic accelerators that enable rubber goods to be vulcanised in a matter of minutes instead of hours, the antioxidants that have so greatly lengthened the useful life of rubber goods, and the reinforcing agents that give the modern motor tyre its amazing resistance to wear, all these are contributions made by chemistry to the rubber manufacturing industry.

Mixing.

Turning now to consider the operations involved in the manufacture of rubber goods by the hot vulcanisation process, which is used in the majority of cases, the first operation is that of mixing into the raw rubber the necessary sulphur and compounding ingredients. To do this the

tough gristly rubber must first be rendered much softer and more plastic than it is in its natural state. This is effected by the so-called "milling" or "mastication" process, which consists in passing the rubber repeatedly between two heated cast-iron rollers revolving at different speeds. When the rubber has been sufficiently softened by the heat and the mechanical action of the rollers, the sulphur and other ingredients are added a little at a time; the repeated passage of the mass through the "nip" between the rollers gradually disperses and grinds the powdery materials thoroughly into the rubber, giving a homogeneous mixture. Recently a different type of mixing machine, called the "internal mixer," has been introduced; in this the rubber mass is kneaded by two S-shaped blades revolving inside a closed chamber, the machine being virtually a large and very massive form of the type of machine used for mixing bread dough.

Shaping the Stock: Moulding, Calendering, Extruding.

The mixture of rubber, sulphur, and other ingredients, known as "stock," has now the consistency of very stiff putty or chewing-gum and must next be formed

into the required shape. The manner of doing this depends on the article being made and the method to be used for vulcanisation. The commonest methods are moulding, calendering, and extruding.

Moulding is usually carried out simultaneously with vulcanisation, and will be referred to later. "Calendering" consists in rolling out the "stock" into a uniform sheet by passing it between the smooth rollers of a "calender." In the extruding process the plastic "stock" is forced through an opening or "die" of suitable shape so as to form it into a rod, tube, or strip of any desired cross-section, the action being very similar to that of the familiar sausage machine.

Rubberised Fabrics.

An important branch of the rubber industry is the manufacture of the rubberised waterproof fabrics used for making macintoshes and other waterproof garments. The commonest method of applying the rubber is by "spreading." The rubber "stock" is softened to a pasty mass or "dough" by adding a solvent such as coal-tar or petroleum naphtha. The cloth is passed between a roller and a knife-like blade which spreads a thin layer of the "dough" on to its surface, after which the coated cloth passes over a heated table to dry off the solvent, leaving a thin film of rubber on the cloth.

Another process, known as "frictioning," avoids the use of any solvent; the fabric is passed between the rollers of a calender, one of which smears on to it a thin layer of the plastic rubber "stock."

Dipping.

Many thin-walled articles like toy balloons, rubber gloves, milk-bottle teats, fountain-pen sacs, etc., are made by the process of "dipping." A former having the shape of the required article is dipped into a solution of rubber in naphtha and



Fig. 8.—"DRY-HEAT" VULCANISING CHAMBERS. Showing batches of waterproof "waders" being loaded in ready for the vulcanising process.

the adhering film of the solution then allowed to dry. Repetition of this process builds up on the former a layer of rubber of the required thickness. Such articles are usually vulcanised by the "cold-curing" process referred to above before

being stripped off the former.

Vulcanising.

The last step in the manufacture of a rubber article is that of vulcanisation or "curing." If the hot vulcanisation process is being used, the article is heated to a temperature usually between 110° and 150° C. for a period of anything from a few minutes to some hours, depending on the composition of the "stock" and the nature of the article. Many articles such as rubber heels, soles, hot-water bottles, rubber cash-mats, door-stops, etc., are moulded to shape and vulcanised simultaneously by pressing the "stock" into an appropriately shaped mould, which is then heated either in an autoclave filled with steam ("pan cure") or between the steam-heated platens of a press ("press cure").

In some cases the use of a mould is dispensed with as being either unnecessary or inconvenient. Thus, rubber floor-coverings are calendered into sheet form and then simply heated between the platens of a large press; rubber tubing, hose, window sealing strips, and other articles made in long lengths are formed into the required shape by extruding and then heated in large steam-filled autoclaves ("open steam cure").

Another method of vulcanisation, used mainly for rubber footwear and rubberised fabrics, is the so-called "dry heat" process, which consists in heating the articles in large chambers filled with hot air.

All the above methods are forms of the "hot" or "sulphur" vulcanisation process. The "cold" vulcanisation process

with sulphur monochloride has been briefly described above and needs no further description here.

Articles of relatively complex structure, such as pneumatic tyres, rubber shoes and boots, fabric-reinforced hose, rubber-covered belting, etc., have to be built up, either mechanically or by hand, from elements prepared by one or other of the processes described above, e.g., calendered sheet "stock," extruded strips or tubes of "stock," rubberised fabric, etc. Thus, a pneumatic tyre cover is made by laying down several layers of a very strong cotton fabric ("cord fabric"), previously rubberised by "frictioning," on a suitable former, affixing to the edges the wire-reinforced "beads," which hold the tyre on to the wheel rim, and finally applying layers of tough wear-resisting rubber "stock" to form the tread and side-walls. The whole is vulcanised in a mould which gives the tyre its correct shape and forms the characteristic non-skid tread pattern. Rubber shoes and boots are built up on suitable lasts, usually by hand, from pieces of sheet rubber "stock" and rubberised fabric, previously cut to shape. Hose is made by extruding a tube of "stock," inserting in this a long metal rod or "mandrel," wrapping layers of fabric around the rubber, and finally applying an outer covering of rubber "stock."

Sponge Rubber.

An interesting branch of rubber manufacture is that concerned with the material variously known as "sponge," "cellular," or "expanded" rubber, and typified by the well-known rubber toilet sponges, "Sorbo" balls, etc. In making these the rubber is compounded with materials that give off gases or vapours when heated (e.g., ammonium carbonate, ammonium chloride plus sodium nitrite, or sodium bicarbonate plus a weak acid). The heat of vulcanisation thus causes evolution of

gas, which expands the plastic "stock" into a spongy form before it becomes vulcanised, just as the carbon dioxide evolved during the "rising" of bread dough produces the well-known spongy structure.

Latex Processes.

It will be realised from the above that the transformation from latex to the finished rubber article normally involves a complicated series of processes, and it is not surprising that attempts have been made to bring about this transformation more directly. These attempts have met with considerable success, so that a number of these direct processes are now being operated commercially. These represent a further striking example of the contributions of chemistry to rubber technology.

Some of the most interesting of these processes depend on the fact that rubber can be electro-deposited from latex in somewhat the same way that metal can be deposited from an electro-plating bath. The rubber particles are negatively charged and therefore collect on a positively charged surface, forming a coherent rubber film. Sulphur and compounding ingredients can be deposited along with the rubber, so that the deposit can be vulcanised by heating. In this way it is possible to make bathing caps, rubber gloves, inner tubes for bicycle tyres, and many other articles, or to form a protective rubber covering on metal or other objects of even the most complicated shape, e.g., wire sieves and screens.

The "dipping" and "spreading" processes referred to above can in some cases be carried out with latex or latex compositions instead of the usual rubber solutions or "doughs," thus avoiding the use of the relatively expensive and highly inflammable organic solvents.

Later articles deal with routine control tests and analyses.

CHEMISTRY AND FLOUR MILLING

PART III.—THE BACTERIOLOGY AND BIOCHEMISTRY OF FLOUR

By THOMAS H. FAIRBROTHER, M.Sc., F.I.C.,

Chief Chemist, McDougalls Self-Raising Flour, Ltd.

FLOUR is a substance that is very susceptible to bacterial infection.

It contains moisture and organic matter and given suitable conditions of temperature an infection soon spreads. Bacteria may be introduced during milling, during storage, or from the excreta of acarids (mites). Kent-Jones and Amos have collected some data on the bacterial contents of various grades of flour. When freshly and normally milled, patent flour contains per gramme less than 20,000 blood heat bacteria, straight run flour less than 50,000, and lower grade up to 300,000 or more. The cool organism content of any grade is nearly always greater than that of the blood heat organisms.

Storage of flour results in a decrease in the number of organisms present, and the rate at which the bacterial content diminishes apparently depends more upon the moisture content of the sample than upon the temperature during storage. The following bacteria have been isolated: *B. mesentericus*, *B. subtilis*, a coccus resembling *staphylococcus aureus*, in addition to several unidentified aerobic organisms.

Kent-Jones and Amos have described the occurrence and isolation of a number of bacteria, photomicrographs of which are reproduced in this article by kind permission of the former.

B. Perfringens.

A large number of experiments were made in an attempt to devise a satisfactory procedure for the determination of the relative contamination of flours with *B. perfringens*. Fig. 1 is a photomicrograph of *B. perfringens* obtained from flour.

This organism is abundant in fæces and, consequently, its presence in a substance is usually considered as an indication of

fæcal contamination. In the case of flour, however, the presence of *B. perfringens*, unless in excessive amount, would not necessarily indicate fæcal pollution of the flour itself, since this organism is found in soil.

Tests for B. Perfringens.

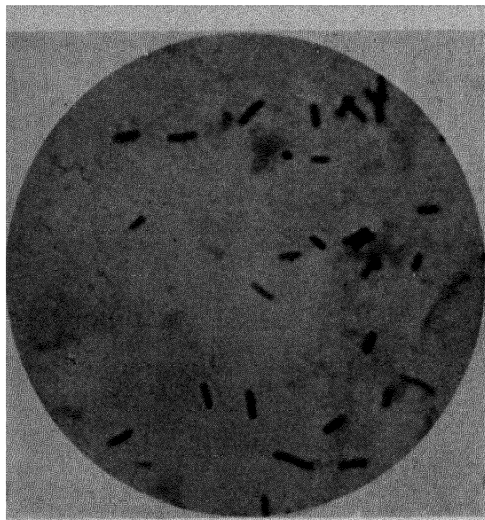
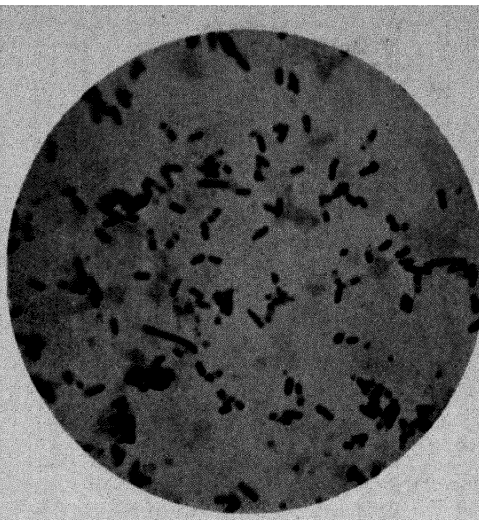
The usual anaerobic milk culture test for this organism was employed. In the early experiments 0.1 or 0.5 gm. of flour and 80 c.c. of sterile skim milk were used, and the time necessary for the production of clot and gas noted. The results were erratic, possibly owing to the occlusion of some of the organisms by the paste at the bottom of the tube, this paste having been formed from the gelatinised starch produced during the heating at 80 deg. C. Rather better results were obtained when 5 c.c. of a 10 per cent. aqueous suspension of flour were added to the milk.

Although this test is not sufficiently reliable to be used as a routine test, it could be used to detect a flour that had received gross fæcal contamination, e.g., contamination with rat or mice dung.

Normal Bacterial Flora of Flour.

Colonies from a number of the plate cultures were examined microscopically as film preparations, and the different types of bacteria were sub-cultured until pure cultures were obtained; these pure cultures were then subjected to cultural, morphological and physiological tests.

In some cases the bacteria responsible for the original colony have been identified, but in others the organisms are still under investigation. The organisms were designated by numbers for convenience, and the numbers missing from the list represented organisms which were later proved to be identical with others already under investigation.

Fig. 1 —*B. PERFRINGENS.*Fig. 2 —*B. MESENTERICUS*

Types of Bacteria so far Examined.

The types of bacteria so far examined are: No. 1, *B. mesentericus vulgatus*; 2, *B. subtilis*; 3, a micrococcus; 4, a cocco-bacillus; 6, *B. mesentericus ruber*; 7, *B. mesentericus fuscus*; 11, a fairly small bacillus; 12, *B. coli communis*. There are, of course, numerous others, not yet investigated, but the above represent the most common and important ones.

"Rope" Organisms.

On account of the frequency of occurrence of these "rope" organisms in flour, an experiment was carried out to determine whether they still existed to any extent in normal loaves. By means of a sterile knife, pieces of crumb were cut from the middle of 24-hour-old loaves and immediately transferred by means of forceps to sterile boiling tubes which contained a little moist cotton wool. These tubes were then incubated at 37 deg. C. Although the flours used in making the loaves varied from the best patent to low grade, and were obtained from six mills in different parts of the country, yet in each case "rope" had developed in less than three days. It should be emphasised that none of these mills was experiencing any trouble in this respect. Further experiments have confirmed this result.

Thus it seems that practically all the bread made in this country, and probably elsewhere also, contains "rope" organisms. The development of the disease in so few instances is accounted for by the

fact that the bread is but rarely stored under conditions sufficiently favourable for rapid growth of the bacteria. For their development these organisms need both moisture and warmth, but, even when these conditions are complied with, the duration of storage is not sufficiently long in most cases. This time factor, of course, is affected by the actual number of bacteria, or rather, spores, that are present.

"Rope" development is greatly retarded at pH 5. It is apparent that, although 40 spores per gm. may be a "reasonable limit" for normal conditions (i.e., time and temperature) of bread storage, in exceptionally hot weather even 10 spores per gm. may be unsafe if the bread is to be kept for several days.

B. Subtilis No. 2.

Colonies of this organism are not infrequent on plate cultures from flour. This is not surprising, since *B. subtilis* occurs abundantly in soil, and is almost invariably found in hay.

Micrococcus No. 3.

This organism (Fig. 3) was found to be present in large numbers on every flour examined. The investigation of this organism to date has yielded the following information:—

Spheres.—Occurring singly and in irregular clumps. Non-motile. Gram-positive.

Gelatin Colonies.—Small, circular, white, entire, slowly liquefying.

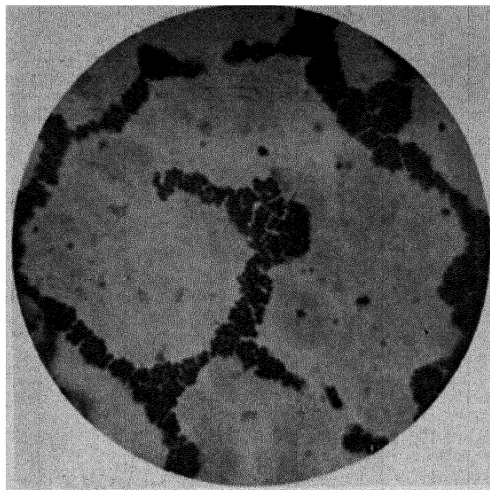


Fig. 3. —MICROCOCOCCUS.

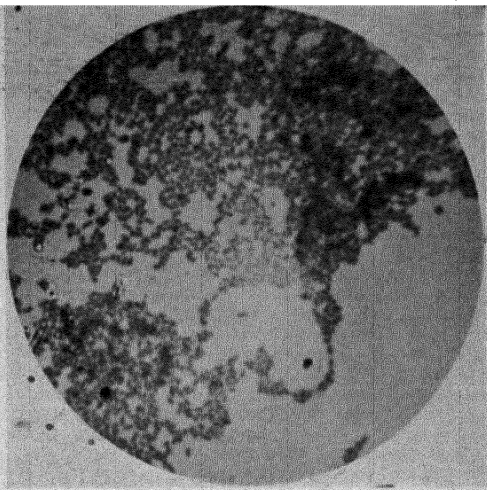


Fig. 4. —COCO-BACILLUS.

Gelatin Stab.—White, surface growth, slow crateriform liquefaction.

Agar Colonies.—Irregular or circular, white, raised, smooth, undulate edge.

Agar Slant.—White, abundant, raised, smooth, opaque.

Broth.—Turbid with viscid sediment.

Litmus Milk.—Decolorised.

Potato.—Moderate, creamy white, raised, dull, smooth, medium, discoloured.

Nitrates.—Not reduced.

Starch.—Is not hydrolysed.

Does not ferment lactose, but develops acid in dextrose and sucrose.

Aerobic.—Grows well at 37 deg. C.

At present no very definite information regarding this organism can be given; the fact that it has been common to every flour examined suggested that it may be of some importance, and so a complete investigation of its properties is being carried out. So far we have failed to find in the literature any specific reference to this common organism.

Cocco-Bacillus No. 4

This organism (see Fig. 4) occurs

very frequently in flour, but more often in the lower grades than in the higher ones. The information so far obtained in respect of this organism is as follows:—

Very small rods and coccoid forms occurring singly. Motile. Gram-negative.

Gelatin Colonies.—Small, brownish-yellow, circular, convex, entire, no liquefaction.

Gelatin Stab.—Yellow surface growth. No liquefaction.

Agar Colonies.—Circular, brownish-yellow, smooth, flat, entire.

Agar Slant.—Abundant, beaded, flat, glistening, brownish-yellow, smooth.

Broth.—Turbid.

Litmus Milk.—Unchanged.

Potato.—Moist, brownish-yellow, medium, discoloured.

Nitrates.—Reduced to nitrates.

Starch is hydrolysed.

Does not ferment lactose, but develops acid but no gas in dextrose, sucrose and maltose.

Aerobic and facultatively anaerobic. Grows well at 37 deg. C.

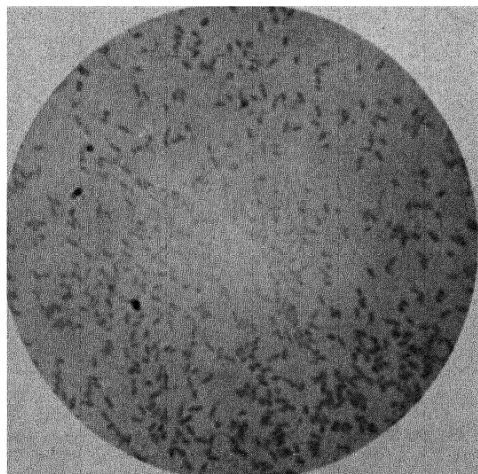


Fig. 5.—BACILLUS NO. 11.

Small Bacillus No. 11.

This organism (see Fig. 5) occurs very frequently in flour, but it only appears on "cool" plates, since it will not grow at 37 deg. C. The following data were obtained:—

Fairly Small Rods.—Motile, gram-negative.

Gelatin Stab.—Napiform liquefaction.

Agar Colonies.—(At 20 deg. C.) Circular, greyish-white, smooth, convex, moist, entire.

Agar Slant.—Greyish-white, moist, smooth, watery.

Broth.—Turbid.

Litmus Milk.—Alkaline.

Potato.—Greyish-white, glistening, smooth.

Nitrates not reduced.

Starch is not hydrolysed.

No acid or gas in lactose, dextrose, sucrose or maltose.

Aerobic.—Grows at 20 deg. C. but not at 37 deg. C.

DETERMINATION OF BACTERIAL CONTENT.

A wide mouthed glass stoppered bottle of 8-oz. capacity, two narrow mouthed glass stoppered bottles of 4-oz. capacity, and a 100 c.c. measuring cylinder are thoroughly cleaned. The cylinder is plugged with cotton wool and placed with the bottles into the hot air steriliser. One 1 c.c. and two 5 c.c. pipettes are cleaned, plugged with cotton wool and inserted in a metal container for one hour at 150 deg. C. A 0.5 per cent. solution of sodium chloride in distilled water is sterilised by steaming for two hours. 100 c.c. of this sterile salt solution is measured into the 8-oz. bottle and 45 c.c. into each of the 4-oz. bottles. 10 gm. of purified sand is ignited strongly in a platinum capsule and poured while hot into the bottle containing the 100 c.c. of salt solution. 10 gm. of wheat or flour is weighed out on a sterile watch glass and transferred into the same bottle. The bottle is shaken vigorously for four minutes for wheat (two minutes for flour).

When the bulk of the sand has settled, 5 c.c. of the suspension is transferred by one of the sterile pipettes into one of the bottles which contains 45 c.c. of the salt solution. The bottle is then shaken vigorously. Then, by means of the remaining sterile 5 c.c. pipette, 5 c.c. of the

liquid is transferred to the remaining bottle, which is vigorously shaken. Finally, 1 c.c. of this is transferred by the 1 c.c. sterile pipette to a sterile Petri dish. A 10 c.c. tube of sterile nutrient agar is poured into the dish. The agar and extract are mixed by rocking the dish, which is then placed on a flat surface till the agar solidifies. The dish is placed in an inverted position in a blood heat incubator (37 deg. C.). A count is taken after 48 hours.

American Method for Bacteria in Flour.

Weigh 0.1—0.5 gm. flour into a small sterile aluminium capsule (20 mm. diameter, 10 mm. high) contained in a sterile glass-stoppered weighing bottle. The tare of the aluminium capsule and weighing bottle is previously obtained. The weighing bottle is opened and the aluminium capsule and flour dropped into 100 c.c. sterile water in a 500 c.c. Erlenmeyer flask. The flask is shaken vigorously to obtain a uniform suspension. 1 c.c. of this is withdrawn with a sterile pipette and added to a tube of wheat flour agar. The medium and suspension are thoroughly mixed by shaking and poured into a Petri dish. The colonies are counted after incubation at the end of 24 and 48 hours.

Bacterial Spores.

100 gm. flour is shaken in 500 c.c. sterile distilled water in an Erlenmeyer flask. Five 1 c.c. samples are added to 5 separate tubes of wheat agar from a sterile pipette. The tubes are then placed in a boiling water bath for 20 minutes. Plates are then made from the agar tubes incubated and the colonies counted after 24 hours.

Determination of Smutty Wheat.

The Federal Grain Standards for smutty wheat require all wheat to be graded smutty which has an unmistakable odour of smut, or which contains spores, balls or portions of balls of smut in excess of a quantity equal to two balls of average size in 50 gm. of wheat.

When the balls become broken and the spores are spread over the wheat kernels, the following test will determine whether the equivalent of two smut balls in 50 gm. of wheat is present. One average sized smut ball weighs .01 gm., and contains

3,750,000 spores. The limit of spores allowed is, therefore, 7,500,000 per 50 gm. wheat.

Apparatus Required.

Compound microscope magnifying 50 diameters, hæmacytometer with Neubauer ruling, i.e., with well $1/400$ sq. mm. in area and $1/10$ mm. deep or $9/10$ of a cubic mm. in volume, an ordinary dropper drawn to a fine capillary point, 500 c.c. Erlenmeyer flask, 100 c.c. volumetric flask and a piece of soft linen cloth.

Determination.

Split the sample to be analysed to approximately 50 gm. and from this weigh exactly 50 gm. By hand pick out all smut balls from the 50 gm. sample and weigh them. Place the 50 gm. sample from which the smut balls have been removed into a 500 c.c. flask. Add 100 c.c. distilled water, stopper and shake vigorously for two minutes. If the count is not to be made immediately, pour the smutty water into another flask as the wheat will absorb much water, thus increasing the density of the spores in the water remaining.

Thoroughly clean the surface of the hæmacytometer with the linen cloth and place the cover slip over the grating so that it rests on the raised guides on each side of the grating.

When the water and smut spores are in thorough agitation draw a small portion of the smut-infested water into the dropper and quickly allow a small portion of the suspension to be drawn under the cover glass by capillary attraction. Care should be taken that there is not an excess of water under the cover glass. If bubbles form start again.

When a satisfactory field is secured, place the slide under the microscope and focus on $1/9$ of the

field. Count each of the nine squares in succession and note the total number of spores present. The number of spores in the field will be the number of spores in $9/10$ c.c. of the water and smut suspension. This number multiplied by 111 will give the number of spores in the 100 c.c. water or in 50 gm. wheat.

Ergot.

Ergot is a fungus which usually attacks rye but occasionally it is found in wheat. The ergot heads vary in size from $\frac{1}{2}$ in. to 1 in. long; the separation, therefore, of complete heads is a simple matter. The danger is when the heads have been crushed and the spores liberated. Under the microscope it appears as a fine network of mostly colourless parenchyma cells containing globules of fat. Some of the cells are circular, others considerably elongated, and some contain a deep brown colouring matter, which with ammonia becomes violet red, changing to red with acid.

Occasionally the cell walls appear of a dark colour. If flour containing ergot be treated with a very dilute solution of aniline violet, the stain will be practically absorbed by the damaged particles of the grain and resisted by the normal granules. A hot alcoholic extract of flour containing ergot is coloured red when treated with dilute sulphuric acid.

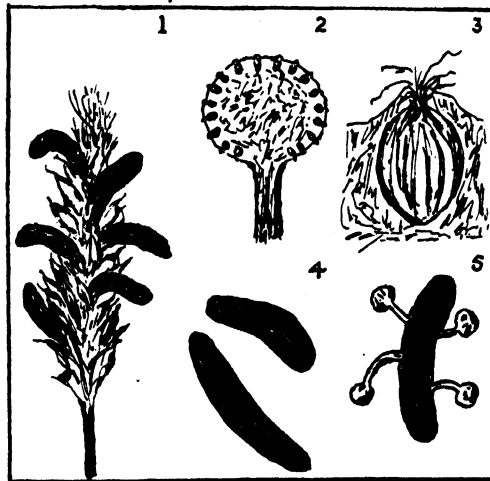


Fig. 6.—ERGOT.

1, Exaggerated drawing of spurred wheat with ergots; 4, loose ergots; 5, ergot sprouting; 2, magnified head of a sprout, showing the spore; 3, magnified spore chamber, showing spores emerging.

THE MICROSCOPIC EXAMINATION OF FLOUR.

This resolves itself into the microscopy of starch. The microscopic examination of flour gives very good indication of grade, whether the grinding has been correct or whether the flour has been subjected to overgrinding. In the lower grade flours the offal can be detected in two ways. Iodine stains the starch cells, but does not affect the

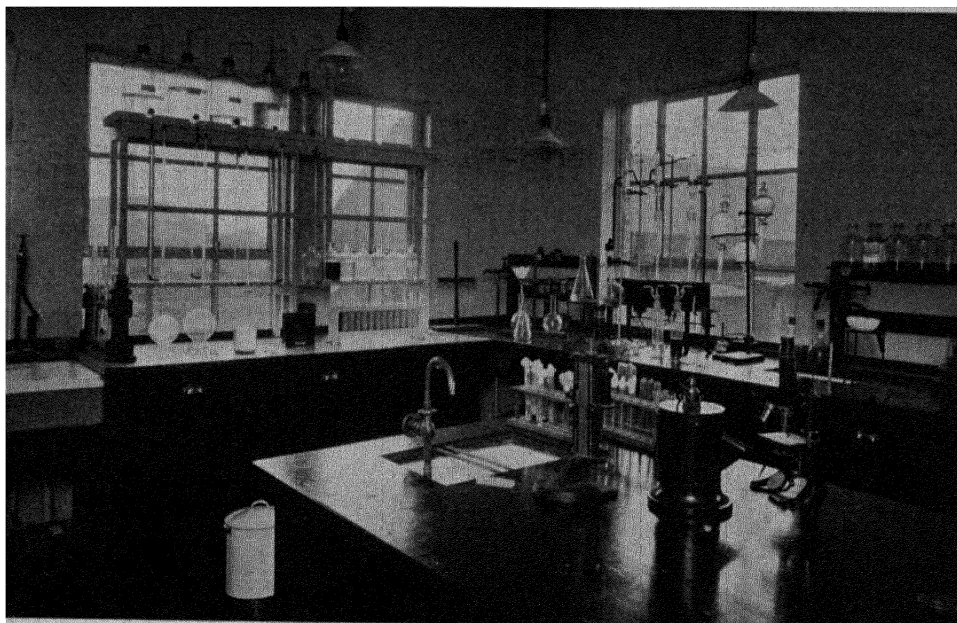


Fig. 7—PART OF A BACTERIOLOGICAL LABORATORY

cellulose. On the other hand, methylene blue stains the ofal blue and leaves the starch colourless.

Preparing the Slide.

The slide is prepared by placing a little flour on a cover slip and distributing it evenly. A drop of the mounting liquid (water is best for direct light and Canada balsam for polarised light) is placed on the slide and the cover slip lowered gently into the drop. This procedure gives a mount free from bubbles.

General Examination.

A general microscopic examination of flour is carried out as follows. The flour is first sieved over a 70 G.G. sieve and the residue carefully examined. The presence of mites, moth, beetle or weevil larvae indicates deterioration by long storage. The sievings are placed in a fine muslin bag and kneaded under water. The turbid liquid is allowed to settle and the solid filtered and air dried. The grains of starch thus obtained are mounted and examined. Damaged flour will show granules partially eaten away by enzyme action and fungal spores may be seen. The bag left after the kneading contains the harder parts of the grain, and gluten. It is emptied into a flask and acetic acid is

added. After standing for several hours the whole is poured into the cloth again and kneading continued until the water leaves the bag clear. The residue contains any characteristic hairs and other structures.

These resistant parts may also be prepared rapidly by boiling with 1 : 20 HCl for a few minutes until the starch is hydrolysed, centrifuging after making alkaline with KOH and finally washing. Careful examination of these residues will indicate adulteration of wheat starch with other starches.

Tests Necessitated by Enzyme Activity.

The chief enzymes which function in bread-making and wheat treatment in general are cytase, which attacks cellulose, diastase, which saccharifies starch, protease, which converts proteins into peptones, and zymase, which is present in yeast along with invertase and maltase.

It is an undisputed fact that diastatic power is directly related to baking strength and flour quality. To quote Rumsey, one of the pioneer workers on diastase, "the flour showing the greater diastatic power should show the greater baking strength and consequently the greater baking value—providing the relative quality and quantity of the gluten is the same." More

recent work, however, shows that there can be too much diastatic activity as well as too little. If the flour has too little diastatic activity the gas production will be low; if there is too much the texture and crumb of the loaf will suffer and there will be an objectionable stickiness and a darkening in colour. The determination of diastatic activity is, therefore, a matter of great importance.

Determination of Maltose Figure.

Thirty gm. flour at 27 deg. C. is mixed with 160 c.c. distilled water at 27 deg. C. and placed in a thermostat, and kept at 27 deg. C. for exactly one hour. The flask is lightly stoppered and shaken every 15 minutes. At the end of the hour the diastatic action is inhibited by adding 6 c.c. of 15 per cent. sodium tungstate solution, acidifying with 20 drops concentrated sulphuric acid and the whole is made up to 200 c.c. It is filtered through a No. 5 Whatman filter paper. The clear solution is placed at once into a burette for titration.

Ten c.c. of the mixed Fehling's solution (plus 1 c.c. extra of the alkaline solution to counteract the acidity of the flour extract) is measured into a conical flask of 250 c.c. capacity and treated in the cold with almost the whole of the sugar solution required to effect the reduction of the copper.

This should be ascertained by a preliminary trial so that not more than 2 c.c. of the flour extract is required to complete the titration. In the ordinary routine work about 25 c.c. of the flour extract can be run in to begin with. The flask containing the cold extract is now heated over a wire gauze standing just under the burette.

After the solution has boiled for exactly 1 minute about 1 c.c. 1 per cent. methylene blue solution is added without removing the flask from the flame. Immediately after the addition of the indicator, still keeping the solution boiling all the time, a little more flour extract is added. This is continued until all the copper is reduced, when the blue of the indicator will disappear. The end point is very sharp.

The maltose figure is read directly from tables, e.g., if 15 c.c. flour extract prepared as above are required for a 10 c.c. Fehling solution, the maltose figure is 3.73; if 50 are required the figure is 1.09.

Gravimetric Method.

The alkaline tartrate solution: 65 gm. NaOH, 175 gm. Rochelle salt per 500 c.c.

The copper solution: 41.2 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per 500 c.c. The clarified extract is carefully neutralised with caustic soda and 25 c.c. of each of the Fehling's solutions is added to an amount which represents 2.5 gm. flour. It is heated at 80 deg. C. for 30 minutes and then filtered through a weighed Gooch with an asbestos mat. After washing with water, alcohol and ether the Cu_2O is dried and weighed.

Picric Acid Method.

This is a colorimetric method and is fairly rapid. In order to estimate the original reducing sugar content of the flour without the occurrence of diastasis during extraction, 5 gm. flour is extracted with 50 c.c. water in an ice bath and filtered. The first few drops are discarded if turbid. 1 c.c. filtrate is added to 2 c.c. saturated picric acid solution and 1 c.c. saturated sodium carbonate solution in a 15 c.c. graduated centrifuge tube.

The tube is placed in a boiling water bath for 30 minutes, during which the reddish colour due to the formation of picramic acid fully develops, the depth of the colour being directly proportional to the concentration of reducing sugar. The mixture is then cooled and diluted to 10 c.c. with water and is compared in a colorimeter with a similarly treated standard solution of pure maltose made up so that 1 c.c. equals 1 mg. maltose. This gives the initial maltose content of the flour.

Another 5 gm. is extracted with 50 c.c. water at 30 deg. C. for one hour, agitating every 10 minutes. After one hour the suspension is settled for 10 minutes and then decanted through a filter and treated as in the ice water extract. The diastatic value is the difference between the two values. The writer has not had much success with this method, as varying colours between red and orange were formed, and in any case a colorimetric method is not to be recommended when a gravimetric one is available.

The writer is indebted to Messrs. McDougalls, Ltd., for permission to publish this article and the photographs of their mill and laboratories.

SUGAR REFINING

PART V.—ANALYTICAL CONTROL TESTS. 4. Moisture ; Dissolved Solids

By H. C. S. DE WHALLEY, M.I.Chem.E., F.I.C.



Fig 1 — THE MOISTURE TEST

10 gm of sample is weighed into a tared dish, placed in an electrically heated Hearson oven, and dried for three hours. It is then removed to a sulphuric acid desiccator, cooled and reweighed. The loss is taken as moisture.

Mixing the Sample.

THE raw sugar sample which is received in a sealed corked bottle is opened, and the whole of the contents transferred to a specially selected sheet of paper. All syrupy lumps are broken up with a flat-bladed spatula and the sample thoroughly mixed and replaced in the bottle. These operations must be speedily effected or moisture content may alter.

This mixing is most essential before any quantities are weighed out for determination of moisture, polarisation, ash, reducing sugar, etc.

How the Moisture Test is Carried Out.

10 gm of the sample is weighed into

a tared flat porcelain dish 3 in diameter $\frac{1}{2}$ -in. deep. The dish is placed in an electrically heated Hearson type oven (Fig. 1), the temperature of which is regulated at 100° to 105° C, and the sample dried for three hours. It is then removed to a sulphuric acid desiccator and cooled and reweighed. The loss is taken as moisture.

Moist syrupy sugars tend to form a hard exterior film on drying which prevents complete loss of moisture.

For these samples an approximately equivalent weight of washed, dried, silver sand is placed in the basin and thoroughly mixed with the sugar to facilitate drying.

Alternatively most of the moisture is removed by drying the weighed sugar at a lower temperature before subjecting it to 100° to 105° C.

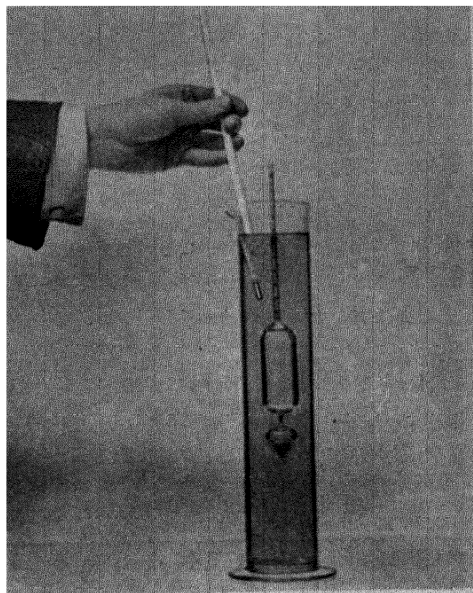


Fig. 2.—THE BRIX HYDROMETER IN GLASS JAR CONTAINING SAMPLE OF SUGAR LIQUOR.

DISSOLVED SOLIDS BY BRIX HYDROMETER.

There are two methods of determining the concentration of dissolved solids in sugar liquors, syrups, etc. The first is densimetric, and the second refractometric.

Densimetric Method by Brix Hydrometer.

The Brix hydrometers are of the glass spindle type, with cylindrical bulb ending in a smaller pear-shaped bulb containing mercury. They are constructed over narrow ranges of density and the interior paper scales in the glass stem are graduated in °Brix (written briefly °Bx). Each hydrometer covers a range of 15 °Bx only. For example 0–15 °Bx is used for sweet waters such as are obtained in washing sugar from filter press cakes, 15–30 °Bx and 30–45 °Bx for lights produced in sweetening-off chas, 45–60 °Bx and 60–75 °Bx for full weight liquors and syrups, 75–90 °Bx for heavy syrups and molasses.

The °Bx at 20° C. of an air free solution of sucrose in water is the per cent. sucrose (dissolved solids) in the solution.

Fig. 2 shows the instrument in a

hydrometer jar with a chemical thermometer to note the temperature.

Temperature Correction.

As the principle of the hydrometer is densimetric the Bx reading is altered by temperature. If the temperature is not 20° C., and it is inconvenient to cool all samples to 20° C., a correction is made. 0.9 °Bx is added to the Bx reading for every 10° C. above 20° C. 0.9 °Bx is deducted from the Bx reading for every 10° C. below 20° C.

°Bx of Low Purity Products.

The hydrometer is calibrated to read per cent. sucrose, but nevertheless, is used for liquors and syrups that contain ash and organic non-sugar which are rather denser than sucrose. The °Bx of lower purity liquors and syrups gives, therefore, only approximately the percentage of dissolved solids. For more exact work refractometric methods are necessary.

Specific Gravity by Brix Hydrometer.

Before leaving the Brix hydrometer mention must be made of the other use which is made of it, viz., as a means of determining specific gravity of liquors, syrups, molasses, etc., for gauging the weight of material held in tanks and barges.

Fig. 3 shows the relation between °Bx and specific gravity. The dip of the tank or barge is taken with a rod graduated in

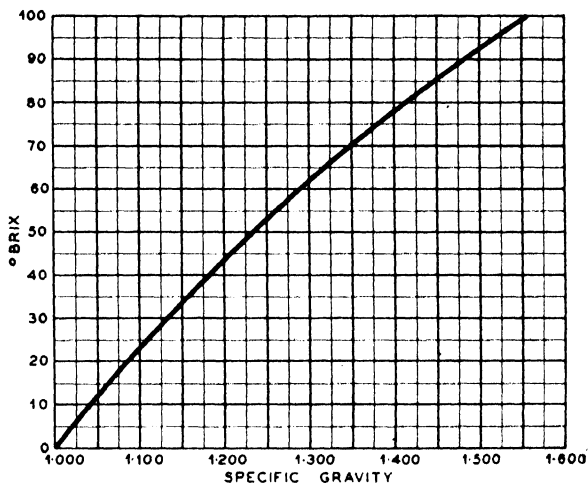


Fig. 3.—GRAPH SHOWING THE RELATION BETWEEN DEGREES BRIX AND SPECIFIC GRAVITY.

feet and inches, and with the area known the volume is computed in gallons.

A sample is drawn and the °Bx read at the temperature of the tank contents, and the specific gravity found by reference to Fig. 3.

The weight in lbs. of contents of tank = gallons $\times 10 \times$ specific gravity. In this case even if the material is much aerated, the gallonage measured has included air, so that the same aerated sample must be

used for specific gravity. When the dissolved solids content is also required the air free °Bx reading at 20° C. must also be taken and the total weight found multiplied by this per cent. dissolved solids divided by 100.

Removing entangled air from a thick syrup or molasses is a long and tedious operation, and recourse is, therefore, made to the more exact method of determining dissolved solids by refractometer.

THE HYDROGENATION OF COAL

THE hydrogenation of coal into petrol is in principle simple. The details of the process have taken ten years and more to work out.

Finely ground-up coal carried as a slurry in heavy oil is heated to 400-450° C. under pressure with an excess of compressed hydrogen at 200 atmospheres pressure. Catalysts such as molybdenum sulphide and tungsten oxide are added to direct the course of the reaction. The yield and character of the final products depend on suiting the temperature of operation and the choice of catalyst to the type of coal used.

Shale and inert matter in the coal has an uncertain influence on the course of the hydrogenation. The coal is therefore first cleaned. It is then rough crushed. Mixed with 50 per cent. of oil it is fed to rod mills which give a thick homogeneous slurry. Pumps compress the slurry to 200 atmospheres pressure and feed it to a coil of pipes in a gas-heated furnace where the temperature is raised to 400° C. Thence the heated slurry goes straight to the continuously operated converter.

Hydrogen is pumped to the converter through heat interchangers where heat is taken from outgoing products. Excess of hydrogen is used to favour the kinetics of the reaction and to volatilise the products of reaction in an atmosphere of hydrogen. Hydrogen is partly provided by recirculated unconverted hydrogen, and partly by a make up of fresh hydrogen from the action of steam on coke.

Heat is evolved spontaneously by the reaction. It is sufficient then to preheat the reactants to 400° C. and to lag the reaction vessel against heat losses.

The products of reaction are petrol,

middle oils and heavy oil which at 400° C. are carried over as vapour volatile in the atmosphere of excess hydrogen. They are accompanied by the "come-down" oil which contains unconverted coal, ash, bituminous products and the original carrier oil. This is separated off in a separator pot kept at the temperature of the converter. It is cooled and centrifuged. The centrifuge gives solid-free oil and a concentrated sludge which is carbonised in steam to get off the oil it contains. This oil with that from the centrifuge is passed back for admixing with fresh coal.

The hydrogen-borne products are passed through a heat interchange unit against the incoming hydrogen. Partly cooled, they are brought down to atmospheric temperature in a water-cooled condenser. Hydrogen bearing gaseous hydrocarbons is flashed off in a separator pot. The hydrocarbons are washed out in a tower scrubber with middle oils as an absorbing liquid. These hydrocarbons are utilisable as "bottled" gas of high calorific value for domestic purposes or for gas engines. The hydrogen is passed back to the compressors for use again in the converter.

The liquid from this cold separator pot is distilled into petrols cut at 175° C., middle oils cut at 375° C. and heavy oils. The middle oils are vaporised, compressed with hydrogen and passed over catalysts to give a high-grade petrol.

The heavy oils from this stage are passed back to be ground into slurry with fresh coal, or used as lubricating oils.

Coal is not always directly hydrogenated. It is sometimes distilled at 600° C., giving smokeless fuel and low-temperature tar, which is then hydrogenated.

THE CHEMISTRY OF NICKEL PLATING

By S. WERNICK, Ph.D., M.Sc.

NICKEL was one of the first metals to be plated commercially. A white, lustrous metal, nickel is tough, wear-resisting and durable, and hence its electrodeposition has created an important industry which has steadily expanded since its inception. This progress has been particularly noteworthy during the past decade, when the tonnage of nickel used by the electroplating industry has probably increased at a greater rate than ever before.

Nickel is, of course, not stainless and it was first thought that the advent of chromium plating some seven years ago, with its obvious advantages, would speedily ring the knell of nickel plating as a finish, or at any rate would seriously affect its popularity. Actually, while chromium plating has undoubtedly replaced nickel plating as a *visible* finish so that perhaps the proportion of nickel plating which can be seen on metal-ware is notably reduced, practically all the chromium plating that one encounters consists of an electrodeposit of chromium over an undercoating of nickel, and the weight of nickel present, although unseen, usually far exceeds that of the chromium.

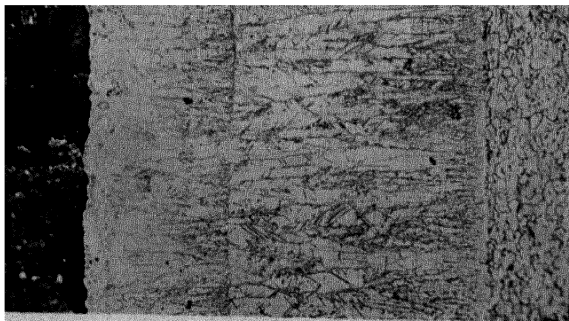
When chromium plating was first applied to metal articles, considerable difficulty was met in producing a chrome finish which would be durable and offer really effective service. After considerable

experiment, it was found that the best chromium plating was obtained when it was deposited upon a compact and non-porous deposit of nickel. It was also found that the nickel so deposited must be particularly good quality plating; otherwise, either the chromium or the nickel, or even both, deposits would readily strip. This fact resulted in considerable research work being carried out in order to establish the best methods of electrodepositing the nickel prior to chromium plating. The net effect has been firstly, that better quality nickel plating is produced to-day than ever before, and this may be obtained at a much faster rate; secondly, more nickel is plated with every fresh application of chromium plating in industry.

Importance of Control in Nickel Plating.

Although nickel plating has been practised for many years, and it is apparently quite a simple process, actually the production of a perfect electrodeposit of nickel is beset by many difficulties. The nickel electrolyte is a sensitive one, and in order to obtain reproducible work of the high standard which is demanded by industrial requirements, particularly when

this must be carried out very rapidly and efficiently, it is necessary to impose very strict methods of chemical control at all stages of the process, particularly, however, those relating to the nickel electrolyte itself.



DEPOSIT (APPROX. $\times 1,000$) SHOWING COMPACT STRUCTURE OF THE COATING.

Constituents of a Nickel Electrolyte.

It will perhaps be recalled (see p. 53) that three of the most important conditions in nickel plating are :—

(1) An adequate concentration of nickel ions in the solution. This may be satisfied by the use of a nickel salt which ionises well. Such a salt is nickel sulphate.

(2) An electrolyte which conducts electricity well. The conductivity of the nickel salt in the solution can be aided by adding further salts which are good conductors, e.g., the chloride of sodium (common salt) or ammonium (salmoniac).

(3) The prevention of co-deposition of substances other than nickel, e.g., hydrogen gas. This may be effected by the use of an acid control, termed a buffering agent, of which boric acid is cited as an example. By preventing the electrolyte from becoming too acid, the evolution of hydrogen at the cathode is restricted as far as possible.

Other Important Constituents.

While the three types of ingredients mentioned above are the most important, one or two further substances are often added because they exercise a beneficial effect. The modern tendency is to reduce the number of constituents in a plating solution to the minimum, since it is then simpler to control it. Occasionally, however, it happens that the same substance exercises a double function. This occurs, for example, in the case of chlorides which are added as conducting salts. It happens that chlorides also aid the corrosion of the anode, the importance of which is explained below.

Oxidising Agents.

Mild oxidising agents are not infrequently added with the object of preventing the growth of organic matter which tends to form in an electrolyte, particularly if it remains unused for any long period. Such substances as hydrogen peroxide (which is innocuous, since it decomposes into oxygen and water) are sometimes added for this purpose. Again, a continuous stream of chlorine gas has been bubbled through the electrolyte in one special process (the Madsenell Process) for the same purpose. Minute quantities of organic matter may have most deleterious effects on the plating both by becoming included in the deposit or by affecting its structure and uniformity.

The use of such oxidising agents is, however, not essential in the production of good quality nickel plating, provided care is taken in the choice of the main ingredients used.

The Corrosion of the Anode.

An elementary consideration of the mechanism of electrodeposition soon makes one appreciate the importance of the correct degree of anode dissolution (or corrosion) as the metal plates out from the electrolyte. As the nickel in the solution becomes exhausted by the continued deposition of the metal, it is necessary that the metal be as continuously replenished so that the metal content remains approximately constant. The nickel which is removed is replaced by that dissolved at the anode, aided usually by the addition from time to time of more nickel salts. Theoretically, of course, the addition of fresh nickel salts should be unnecessary, but in practice the anode is seldom found to dissolve with 100 per cent. efficiency, i.e., strictly in accordance with Faraday's Laws.

Most usually, the anode efficiency falls short of this ideal, since the current may be dissipated in directions other than the dissolution of nickel, e.g., in the production of oxygen. It is therefore necessary to add a substance which will aid the corrosion of the anode. Sulphuric acid acts in this manner, but the addition of any acid to the electrolyte must be made with great caution since it will affect a property which is known as the *pH* of the electrolyte, the quantitative value of which is very critical and directly affects the quality of the electrodeposit.

More commonly, chlorides are added to effect anode corrosion, the anion, Cl (the chloride ion) being extremely active in attacking the nickel anode. One of the best chlorides to use is nickel chloride, since not only does it furnish active, nascent chlorine at the anode, but in addition furnishes nickel ions directly in the electrolyte. The chlorides of sodium and ammonium (which it will be recalled are additionally valuable as conducting agents) are also very widely used. They are both efficient and cheap anode corroding agents.

Effect of the Anode Efficiency on the Acidity of the Electrolyte.

In a rough way, nickel platers have from

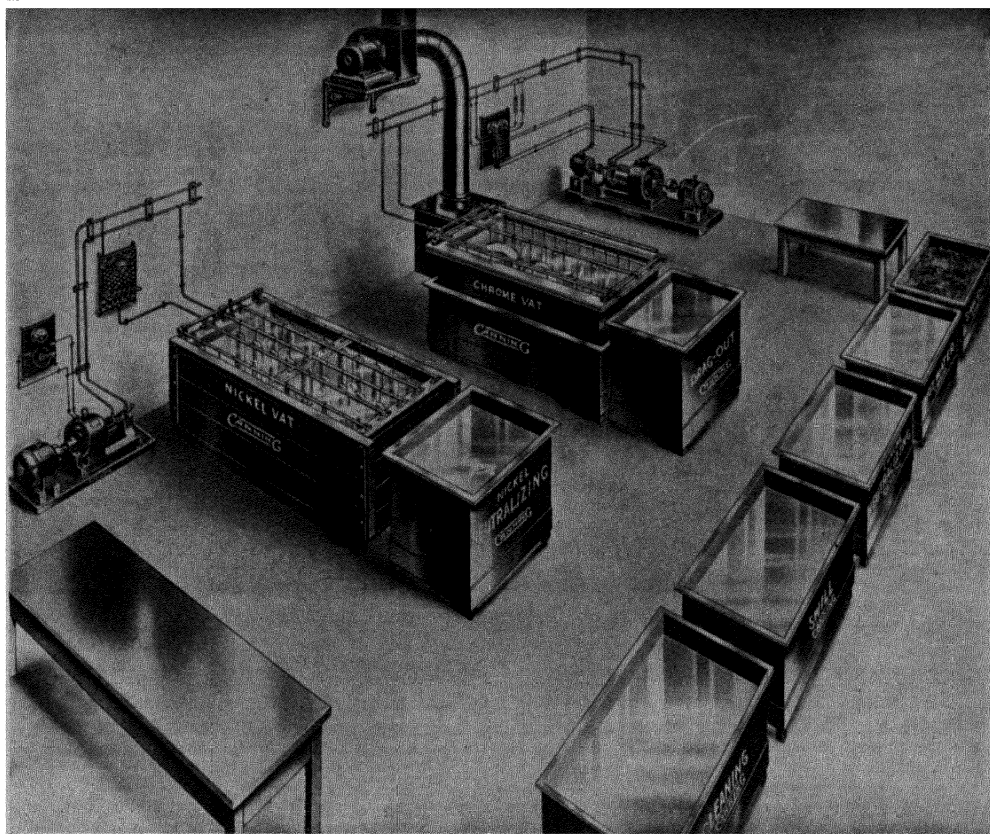


Fig. 2. —DIAGRAMMATIC LAYOUT OF A PLANT FOR PRODUCING NICKEL PLATING PRIOR TO CHROMIUM PLATING.

Showing the necessary washes, rinses, etc., as well as the electrical equipment.

earliest times realised the vital influence of the acidity of their solutions, and at first tried to control this in a crude manner by periodic determination of the acidity, using "test papers"—generally litmus paper, which turns red in acid, and blue in alkaline solutions. In this way it is possible to ascertain whether the solution is definitely acid or alkaline, but the amount of acid present, and the extent of this acidity (which, be it noted, are two entirely different things, as will be shown presently) cannot be inferred from the colour of the test paper.

It is possible in a crude way to say whether the solution is "very acid" or only "slightly acid," by noting the degree of redness in the test paper, but the most that can be said of this method of testing the acidity of nickel-plating solutions is that it is rather better than no test at all and that it involves very little time or

expense in its application. It must, however, be emphasised that the test is not sufficiently sensitive to provide even a fairly approximate control of the acidity of the solution.

The two terms "amount of acid present" and "acidity of the solution" which have just been differentiated, appear to be so similar that there is some little difficulty at first in grasping wherein this difference lies. The conception of this difference is, however, important and one which the nickel plater now fully realises. It is the basis of one of the most important routine tests carried out in connection with nickel plating practice—the determination of pH .

The Hydrogen Ion—An Important Constituent.

The all-important constituent of all acids is the hydrogen ion, and when an acid is diluted with water, or added to any

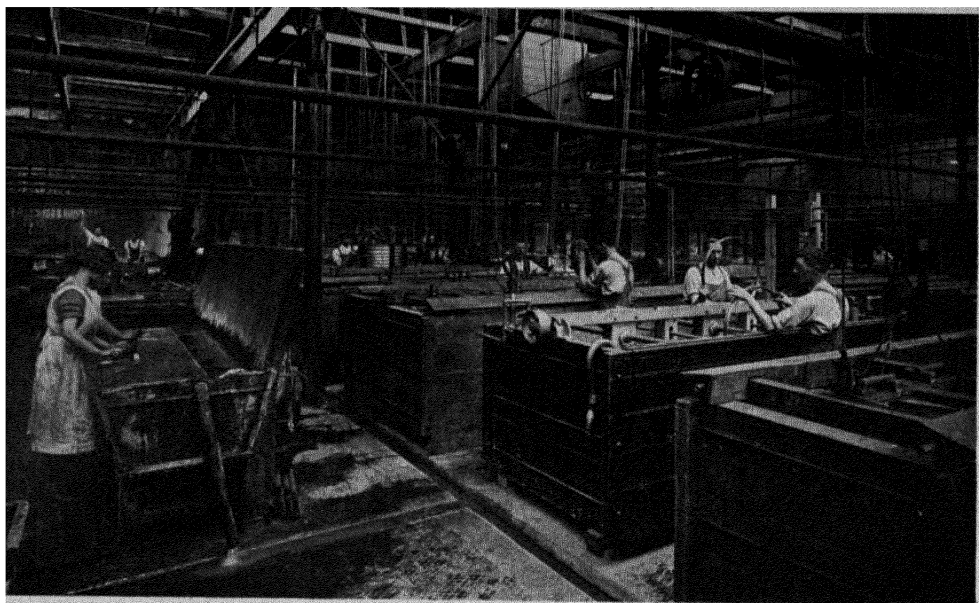
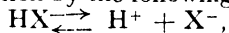


Fig. 3—THE NICKEL-PLATING DEPARTMENT OF THE RALEIGH CYCLE FACTORY

aqueous solution, it dissociates, or breaks up into this hydrogen ion and the remaining radicle. If we denote any acid by the formula HX , where H is the hydrogen ion and X the radicle determining the nature of the acid, then we may express the dissociation by the following equation:



the H having a positive and the X a negative electric charge, while the arrows indicate that the reaction is reversible and the dissociation incomplete.

The extent to which this dissociation proceeds determines the "strength" of the acid, and thus the terms "strong acid" and "weak acid," which are frequently encountered, are respectively meant to convey the idea of acids which are very much, or very little, dissociated in solution. Examples of the former are hydrochloric and sulphuric acids; of the latter, boric and acetic acids.

In general, the greater the degree of dissociation of the acid, the more active it is. The degree of this dissociation is not necessarily related to the amount of the actual acid (i.e., the amount of HX) present, and, in point of fact, the smaller the quantity of the acid present in solution, or, in other words, the more dilute the acid solution, the greater is the degree of dissociation in the case of a *given acid*.

But solutions containing the same

amount of *different* acids may vary very considerably in the hydrogen ion concentration. The two terms, "concentration of acid present" and "hydrogen ion concentration," are, therefore, entirely different. While the former gives the actual *quantity* of the acid present, the latter may be considered to indicate the *quality* of the solution in so far as its acidity is concerned.

A "Normal" Solution.

A solution is considered to be "normal" in respect of hydrogen ions when it contains one gramme of these hydrogen ions per litre. It is one-tenth normal when it contains one-tenth gramme in the same volume, one-hundredth normal when containing one-hundredth gramme, and so on. The solutions commonly used in nickel plating contain only a very small hydrogen concentration of the order of $\frac{1}{100,000}$ to $\frac{1}{10,000,000}$ normal, i.e., $1/10^5$ N. to $1/10^7$ N. Since it is somewhat awkward to write, or speak, of concentrations in these low fractions, the indicator in the denominator (5 and 7 respectively in the above cases) is the figure selected to express this value, and this figure is known as the "*pH* value of the solution." In the cases quoted, the acidity of the two solutions is, therefore, expressed as *pH*5 and *pH*7 respectively. It is necessary to note that, although a

higher number is assigned to the latter, on referring back to the fraction it denotes, this actually is seen to be lower than the former figure. In other words, the *higher* the pH value, the *less* the acidity.

Now, as the acidity decreases, we arrive at a point where the solution is considered to be neutral, and on lowering the hydrogen ion concentration still further the solution becomes alkaline. This neutral point is approximately at a pH of 7. It happens that litmus changes colour at about this pH so that all that can be inferred from a change in its colour is that the pH is not above 7 (i.e., alkaline), and that it is probably below about 6.5. Since nickel-plating solutions must be kept at a pH ranging as a rule from 5.2 to 6.5 (depending on the type of solution) this information is obviously insufficient.

Where Greater Accuracy is Desirable.

We may use an indicator which changes its colour at a lower pH value, e.g., Congo red (or "Congo paper"); this changes from a scarlet to a blue colour between pH_3 and pH_5 and would serve to indicate when the solution was becoming too acid, but still would not inform us of the precise state of acidity of the solution. *In general the colour change of indicators is over too wide a range of pH to enable them to be effectively used by merely dipping the paper-coated indicator into the solution, and observing the resultant colour change.*

Determining the pH Value of Coloured Nickel Solution.

There are two means at present of ascertaining the exact pH value of the coloured nickel solution. The first is an electrical method—the quinhydrone electrode—which is by far the more accurate of the two. It is rarely used in connection with work in the plating shop, however, not only on account of its prohibitive cost but because the second method is much simpler and quite accurate enough for most purposes.

The Colorimetric Method.

This second method is a colorimetric one, by which a colour change is effected in the nickel solution by adding a specific indicator and this is then compared with standard solutions of known pH which

have been similarly treated with the indicator. The apparatus required for this is essentially a so-called "comparison block" containing 9 holes, arranged 3 by 3, to take 9 small glass tubes, while 3 small "sight" holes are bored through from one side to the other at right angles, one side being fitted with a piece of ground glass. (See Fig. 5.)

In addition, a rack is required to hold a series of tubes, containing acid and alkali in known proportions, pairs of these tubes giving a series of pH values, say, from 5.3 to 7.0. The indicator used is Brom-cresol-purple, giving a range of colours from pH 5.3 to pH 7.2, and on adding varying fixed quantities of this to the prepared tubes, a series of colours is obtained.

Apparatus Both Simple and Effective.

In determining the pH , 5 c.c. of the nickel solution to be tested is placed in each of the tubes numbered 7, 8 and 9 shown in the illustration. A given quantity of the indicator is added to tube 8, distilled water placed in tubes 2 and 5, and two pairs of tubes of known pH placed in tubes 1 and 4 and 3 and 6 respectively; these, say, have respective pH 's of 5.5 and 7.0. On looking through the view holes the shade of number 8 is seen to be between those of Nos. 7 and 9. Other pairs of tubes of known pH are then substituted in the holes on either side until the colour of tube 8 is matched, this being the pH required.

Although from this brief explanation this method of determining pH values may appear to be complicated, in reality it is a perfectly simple operation when everything is ready to hand and the test can be carried out in a matter of a few minutes. The apparatus required is simple and inexpensive, and can either be purchased or made.

The apparatus is not only useful in determining the acidity of a given solution, but by its aid it is possible to ascertain how much acid or alkali it is necessary to add (as the case may be) in order to bring it back to normal pH at which the solution should work. All that is necessary is to add progressively, to a small given volume of the solution, known amounts of the acid or alkali, determining the pH of the solution at each stage until

the requisite acidity is reached. It is then merely a matter of multiplying the amount of neutralising material used by the ratio between the solution which has been employed and the volume of the vat, and then adding the resultant quantity of chemical to the electrolyte.

The pH of a nickel-plating solution is highly important, as it directly affects the character of the deposit. If the pH is low, copious "gassing" or evolution of hydrogen occurs at the cathode, and this results in a very poor type of deposit which is pitted, if the pH is high, then the deposit may become dark, streaked and brittle due to the precipitation of basic salts in the vicinity of the cathode. Thus, the range of pH which is productive of deposits of good quality is limited and fairly narrow. It extends roughly, under ordinary conditions, from a pH of 5.2 to 6.3, although under very special conditions, good deposits may be obtained outside this range.

Connection Between Anode Dissolution and pH .

The rate of solution of the anode has a most important bearing on the pH of the electrolyte, as may readily be appreciated by considering two cases, in one of which the anode is not sufficiently soluble, while in the other, the solution rate exceeds that of deposition.

In the first case, more nickel is being deposited from the solution than is being

replenished by the anode. This has to be made up by the addition of nickel salts to the solution at more frequent intervals or in greater amount than is ordinarily required. So much for the effect of the cathode side. But we also have to consider that the electrolytic reaction at the anode is also not proceeding at a sufficiently fast rate. In other words, the SO_4 ions released at the anode are not reacting with the nickel to the extent they should.

They, however, are able to unite with hydrogen ions in place of the nickel, and in so doing form sulphuric acid. The net result is an increase in the acidity of the solution, small variations in which it should be remembered may easily upset the equilibrium of the bath. The effect, however, does not end here.

In the second case, where the anode dissolves at a rate appreciably faster than its appearance as nickel plate, the results are

equally unsatisfactory. The solution becomes overloaded with nickel ions, and these encountering a scarcity of SO_4 ions (with which it will be remembered they join to form nickel sulphate, $NiSO_4$) accordingly react with the molecules of sulphuric acid present in the solution, and therefore reduce the content of free acid.

Controlling Rate of Dissolution.

If the difference between anode rate of solution and cathode rate of deposition

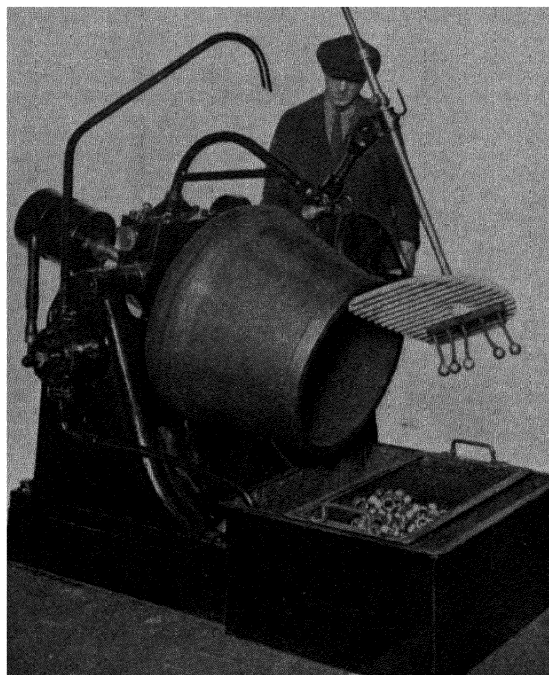


Fig 4—A BARREL PLATING UNIT IN WHICH SMALL ARTICLES ARE PLATED WITHOUT BEING WIRED TOGETHER

They are rotated in the barrel and make contact through one another with the cathode (the metal balls in the picture)

is large enough, the bath after a short time will become markedly alkaline. Acid must be added to replenish what has been used. Meantime, the congestion in the solution in the case of a bath already rich in nickel salts may result in the precipitation of the excess salts from solution; while a sufficiently alkaline solution will not only produce a poor deposit, but may even codeposit with the nickel a green basic salt upon the "work" plated.

How, then, is the rate of dissolution of the anodes to be controlled? It happens that the rate is dependent to a great extent upon the physical condition of the anode. A *cast* nickel anode is extremely porous as compared with a *rolled* anode, and, therefore, presents a far larger area to the solution. Thus it is more rapidly corroded than the rolled anode. Indeed, the difference is so marked that, while the sole use of rolled anodes in a vat will cause increased acidity, cast anodes tend to make the solution alkaline.

By a judicious use of the two types of anode, it is thus possible to arrive at a condition where the acidity of the bath is comparatively unaffected by the anodes. In general, satisfactory results are obtained by hanging rolled and cast anodes alternately in the solution.

Types of Anodes in Use.

Apart from cast and rolled anodes, other types of anodes have recently come into use by the plater. It is essential to keep the electrolyte as free as possible from impurities since in any appreciable quantity—and in the case of some impurities, even when present in quite minute quantity—they have a detrimental effect on the deposit. The salts dissolved in the solution are, therefore,

as commercially pure as possible, and the anodes, too, must be of a high degree of purity. The purest type of anode which can be used is one which is itself produced by electrolysis. The electrolytic anode which is produced when nickel is electrolytically refined contains only a small fraction of 1 per cent. of elements other than nickel, and is, therefore, little likely to introduce "foreign" impurities in the solution. It is produced in relatively thin slabs and is generally used by the plater in the form of rectangular plates of suitable size.

One difficulty which is associated with these electrolytic anodes is their tendency to become "passive," or non-reactive—this being a characteristic of many metals in a high state of purity. In this condition, the anode refuses to dissolve freely. Fortunately, it is readily possible to overcome this tendency by the use of chlorides in the solution, smaller quantities of fluoride being sometimes additionally added since the effect is then more marked.

A second interesting type of anode is termed the "depolarised" or "depassive" anode. This type of anode again consists of highly pure (99-100 per cent.) nickel to which has been added during the casting process a very small proportion of nickel oxide. These anodes are usually subsequently rolled into the form of oval-shaped rods and, in the presence of chloride in the electrolyte, they are found to dissolve satisfactorily, the small addition of oxide aiding the uniform corrosion of the anode.

CHEMICAL ANALYSIS OF ANODES.

The deleterious effects of impurities in the anodes on the quality of the deposit are so marked that it is important to specify the limiting quantity of impurity

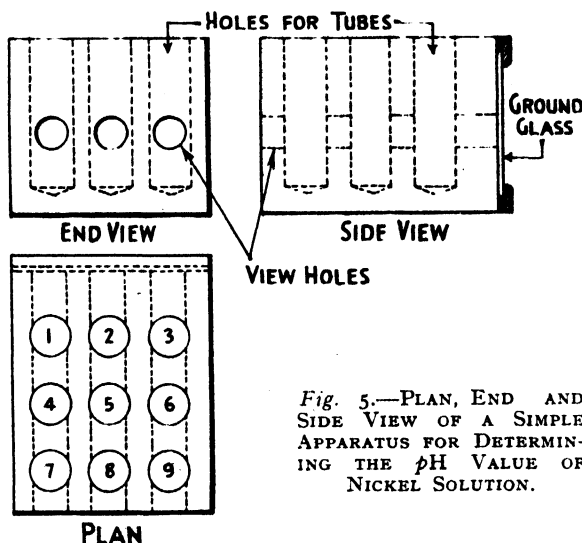


Fig. 5.—PLAN, END AND SIDE VIEW OF A SIMPLE APPARATUS FOR DETERMINING THE pH VALUE OF NICKEL SOLUTION.

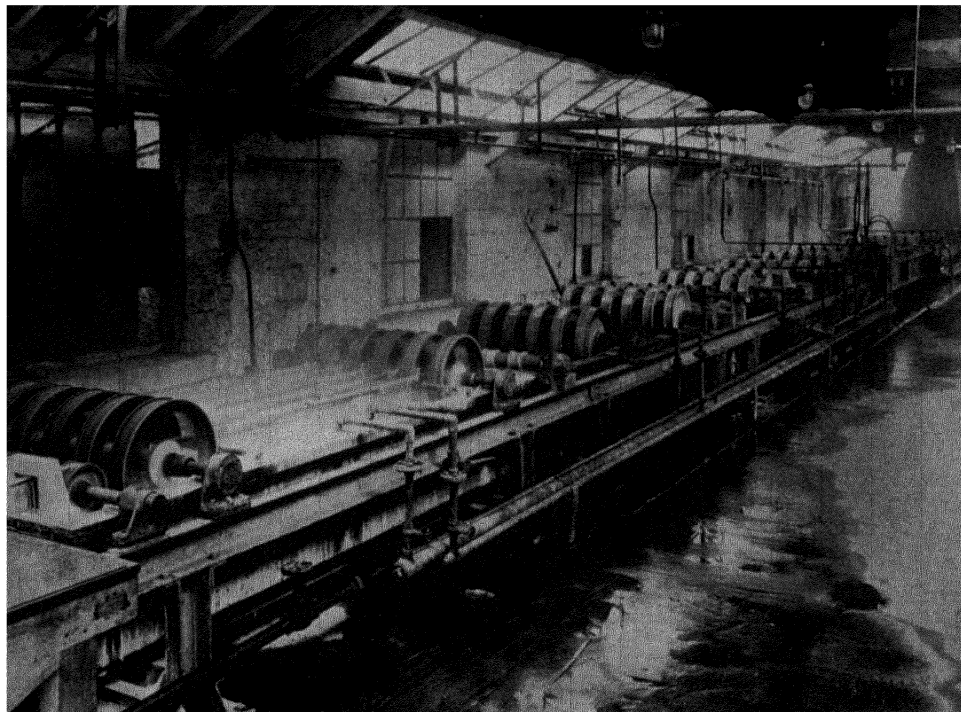


FIG. 6. SPECIAL PLANT USED FOR NICKEL PLATING THE RIMS OF CYCLE AND MOTOR-CAR WHEELS

permissible in the anode. This matter was exhaustively studied by the British Standards Institution, who have recently issued a specification on the subject which limits impurities in nickel anodes to the following amounts: iron, 0.75 per cent.; copper, 0.25 per cent.; silicon, 0.10 per cent.; manganese, 0.10 per cent. and carbon 0.3 per cent. The percentage of nickel present must, however, in any case, not be less than 99 per cent. It is, however, well known that cobalt is closely associated with nickel in nature, and since no disadvantage accrues from the presence of cobalt in small quantity, 0.5 per cent. of this metal is allowed to be included in the 99 per cent. of nickel.

In making a test, a sharpened twist drill is used which has been thoroughly cleaned in petrol and wiped clean with muslin. The anode is freed from any loose impurity by means of a steel wire brush, and a hole is bored which is approximately 10 per cent. of the thickness of the anode, the drillings being discarded. The anode is now placed on a clean piece of paper and

a further 80 per cent. of the thickness is now drilled, these drillings being collected and transferred to a clean container. The drillings are then washed in petroleum spirit and are now ready for chemical examination.

The chemical analysis is conducted as follows:—

Determination of Silicon.

Dissolve 5 gm. of drillings in diluted nitric acid (sp. gr. about 1.3) and cool when the reaction is complete. Add 20 c.c. of sulphuric acid (sp. gr. 1.84) diluted with an equal volume of water, and evaporate the liquid to fuming point without boiling. Nickel sulphate then separates as a solid cake and not as a powdery mass liable to cause "bumping." When the salts have separated and the liquid is nearly colourless the beaker can be moved to a hotter part of the hot plate and heated strongly to fuming for three or four minutes. Add about six volumes of water and move the beaker after cooling to a cooler part of the plate. Boil the

liquid to hasten dissolution of the nickel salts. If appreciable quantities of lead are present, lead sulphate will be seen on the bottom of the beaker. If no lead sulphate is seen, filter the silica rapidly from the hot solution and wash with water until free from nickel salts. Ignite the impure silica in a platinum crucible, weigh and treat with a little pure hydrofluoric acid and a drop or two of strong sulphuric acid and evaporate to dryness. Ignite the residue and weigh. The difference between the two weighings represents silica and the silicon can be calculated from this difference.

Determination of Copper.

If no lead sulphate is seen in the estimation of silicon, then the filtrate from the silica should be neutralised and acidified with 4 c.c. of diluted hydrochloric acid (sp. gr. 1.1) for each 100 c.c. of liquid. Pass the hydrogen sulphide gas to saturation; filter the sulphides and wash with water saturated with hydrogen sulphide and treat the precipitate and filter paper with nitric acid (sp. gr. 1.4), concentrated sulphuric acid and water and evaporate down to fuming. Filter the lead sulphate on a Gooch crucible, weigh, and extract with ammonium acetate, and determine the copper in the filtrate electrolytically, colorimetrically, or by precipitation as sulphide and ignition to oxide if small in amount.

Determination of Iron.

Boil the filtrate from the copper sulphide to expel the hydrogen sulphide and the iron is oxidised by boiling with bromine water. Precipitate by ammonia the hydroxides of iron (and aluminium); redissolve the precipitate in dilute hydrochloric acid and re-precipitate by ammonia. If the precipitate is small, it is ignited and considered to consist of Fe_2O_3 wholly. If it amounts to more than a milligram or so, redissolve it in dilute hydrochloric acid, and titrate the iron with titanous sulphate solution.

Determination of Manganese.

Determine on a separate portion of 1 to 2 gm. drillings or pieces, by dissolving the metal in nitric acid sp. gr. 1.2, containing some hydrochloric acid. The proportion of hydrochloric acid depends upon the rapidity of the action of the nitric acid. When dissolution is complete,

evaporate down to a pasty consistency, add nitric acid and boil to expel chlorine. If necessary, repeat. Add 100 c.c. of nitric acid sp. gr. 1.4, raise to boiling to expel oxides of nitrogen, drop in a little at a time 5 gm. of potassium chlorate. After the addition of the chlorate, evaporate the liquid to small bulk (about 25 c.c.), add 40 c.c. of water to cool rapidly. Filter rapidly through an asbestos-packed filter and wash the precipitate of hydrated manganese peroxide with cold colourless strong nitric acid. Place the asbestos and precipitate in a beaker, with a little water, add a little nitric acid and some saturated solution of sulphur dioxide, boil to expel the excess of sulphur dioxide, filter from the asbestos, cool and add 1 gm. of solid sodium bismuthate. Stir for a few seconds and filter rapidly through asbestos, or an alundum cone, or sintered glass crucible. To the filtrate add an excess of N/20 ferrous ammonium sulphate and titrate the unused ferrous iron with N/20 potassium permanganate. The ferrous iron is then calculated with N/20 potassium permanganate and the equivalent of manganese may then readily be calculated.

Determination of Carbon.

Two or three gm. of drillings in very small pieces is placed in a 400 c.c. tall beaker. The metal is covered with a mixture of 200 c.c. of saturated potassium (or ammonium) cupric chloride and 15 c.c. of hydrochloric acid sp. gr. 1.16. The liquid is stirred for a few minutes and the covered beaker is placed in a water bath kept at about 50° C. It is desirable to stir the liquid frequently, preferably by means of a more or less continuous automatic device in order to hasten the dissolution of the nickel and precipitated copper. When the nickel has dissolved completely (ascertained by disappearance of hard pieces) the carbon is filtered off through an asbestos-packed Gooch crucible and washed with hot water. The asbestos must have been prepared by boiling with hydrochloric acid and subsequent ignition. The asbestos and carbon are transferred to a suitable combustion boat, any carbon on the sides of the crucible being wiped off with a wad of damp asbestos and added to the main bulk. The boat is dried at 90° to 100° C., and the carbon determined by combustion and weighing of the carbon dioxide formed.

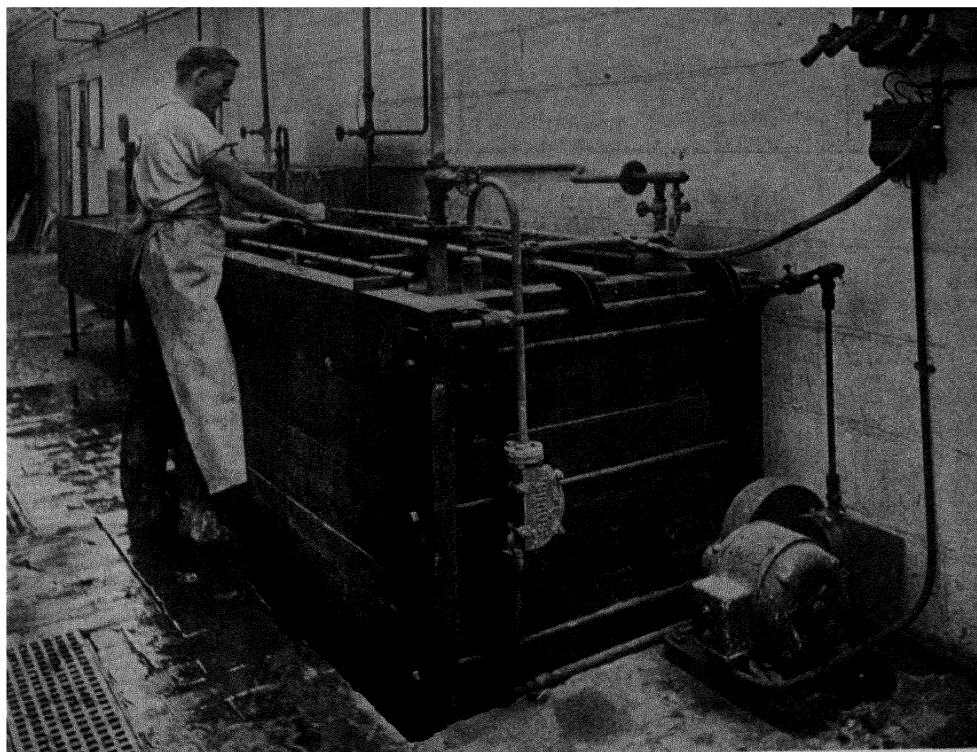


Fig 7—THE AGITATOR DRIVE TO THE NICKEL VAT WHICH KEEPS THE SOLUTION CONTINUALLY AGITATED

Analysis of Nickel Salts Used in Electrolyte.

In a very similar manner to the above procedure, the determination of impurities in the nickel salts which are dissolved in the solution is carried out. It will be remembered that the most important of these salts are nickel sulphate, nickel ammonium sulphate and nickel chloride. The main impurities here are iron, copper and zinc, the presence of which is limited to very small quantities—of the order of 0.01 - 0.1 per cent, zinc being actually limited to 0.01 per cent.

Analysis of a Nickel Plating Solution.

The composition of the nickel plating solution is determined at regular intervals, the practice obtaining in most works being a routine test approximately weekly, although the pH usually requires to be taken daily and where heavy production is involved, even more frequently.

Usually, the density of the electrolyte provides a useful though not an infallible clue to the nickel content of the solution. The simplest method by which the nickel

concentration is determined is by electrolysis. 25 c.c. of the nickel solution is abstracted and about 5 gm. of ammonium sulphate and about 25 c.c. of strong ammonia are added, the whole being diluted to 200 c.c. The solution is then electrolysed for about one hour in a beaker using an anode of platinum and a rotating cathode of copper, the current density being about 2 amp/dm² and the solution being stirred throughout. The blue colour of the solution gradually disappears and in order to ascertain whether all the nickel has been deposited, a drop is taken out, and to it a drop of a 1 per cent alcoholic solution of dimethylglyoxime is added. The electrolysis is continued until this test no longer produces a pink colour (showing complete absence of nickel). The cathode is then washed, dried and weighed, the increase being the amount of nickel present in 25 c.c. of the original solution.

The chloride content may be determined either gravimetrically or volumetrically. By the former method, a quantity of the solution is diluted about ten times and a

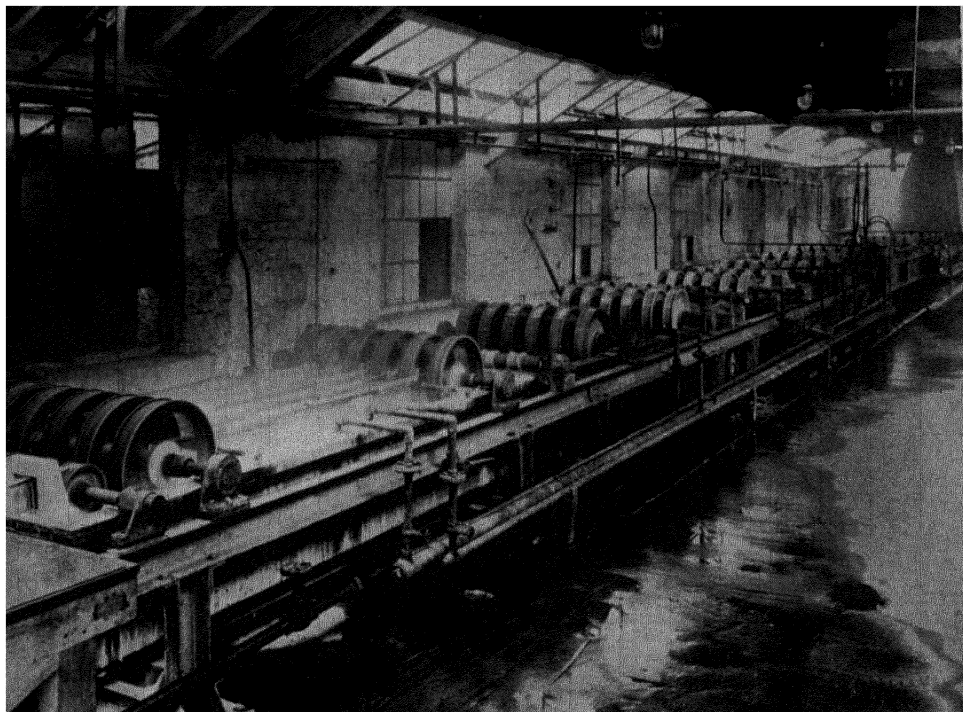


Fig. 8.—THE CENTRAL PORTION OF AN AUTOMATIC NICKEL PLATING PLANT AT THE WORKS OF THE AUSTIN MOTOR CO., LTD.

Showing the rotary air pump for agitation and filtration and the electrical equipment.

few drops of nitric acid added. After the solution has been heated to boiling, an excess of silver nitrate is added, and after standing, the precipitate of silver chloride is filtered on a weighed Gooch crucible which is then dried and reweighed. The chloride content is then readily calculated from the formula :—

$$Cl = \frac{S}{143.3} \times 35.5 \text{ gm./litre, where } S =$$
 silver chloride precipitate resulting from 1 litre of the electrolyte (calculated pro rata from the quantity actually used in making the test, e.g., if 20 c.c. used, multiply the weight of precipitate by 50 to obtain S).

Apart from the pH determination, the other substances present are not critical, e.g., boric acid, etc., but methods for determining the latter are available, although they are necessarily more complex.

Operating Conditions.

Modern methods of mass production

which exist in most up-to-date factories have resulted in the development of means whereby high-speed nickel plating is produced which, nevertheless, is of excellent quality. Some 15 or 20 years ago, the type of nickel solution employed was relatively low in metal content; the conductivity was therefore poor, and since the electrolyte was "worked cold," i.e., at ordinary temperatures, the current density which could be used was small. The deposition of an adequate thickness of nickel was, therefore, a lengthy business. By "adequate thickness" is meant a deposit of the order of one-thousandth of an inch, and this would take some three or four hours to produce at the current densities of 5 to 8 amps. per square foot, which were commonly practised at that time. The manner in which the rate of deposition of nickel varies with current density may be worked out by Faraday's formula (see p. 52); for convenience it is tabulated here for C.D.'s (current densities) between 3 and 100 amps./ft.².

Table Showing Variation of Thickness of Deposit with Current Density and Time of Deposition.

Current Density (amps./ft. ²).	THICKNESS OF NICKEL DEPOSIT (inches).			
	$\frac{1}{2}$ hour.	1 hour	2 hours	3 hours
3	0.00008	0.00017	0.00034	0.00050
4	0.00011	0.00022	0.00043	0.00065
5	0.00014	0.00028	0.00055	0.00083
7.5	0.00021	0.00041	0.00083	0.00124
10	0.00028	0.00056	0.0011	0.0017
15	0.0004	0.0008	0.0017	0.0025
20	0.0006	0.0011	0.0022	0.0034
25	0.0007	0.0014	0.0028	0.0042
50	0.0014	0.0028	0.0056	0.0084
100	0.0028	0.0056	0.0112	0.0168

Modern Improvements.

By the introduction of modern methods, which have been developed in recent years, current densities up to 100 amps. per sq. foot are not uncommon. At 50 amps./ft.², which it would have been impossible to apply under the old conditions without obtaining "burnt" and entirely valueless deposits, one may plate 0.001 inch in about 20 minutes, which is equivalent to a speed-up of 500 to 1,000 per cent. The principal improvements which have been introduced to effect this speedier production are the use of an electrolyte carrying a high metal content, the heating of the solution, its agitation and, finally, filtration. In order to cope with this increased plating speed, automatic plant has been introduced and is now widely used to reduce the manual work as far as possible.

Method of Heating the Solution.

The solution is heated to a temperature of about 50° C. to 60° C. and this increases its electrical conductivity, permitting the passage of the higher currents employed. The heating may be effected by either steam, gas or electricity and all of these methods are commonly employed. The steam heating is effected by the use of lead pipes which are laid at the bottom of the plating tank; electrical heating may be neatly employed by similar means, the enclosed element being coiled on the floor of the vat. The gas heater is most con-

veniently attached to one of the smaller ends of the tank. The most economic form of fuel is largely dependent on the costs ruling in the particular district.

The electrolyte is then agitated mechanically, the effect of this being to bring up fresh lots of solution in contact with the cathode so that the layer nearest the latter is always rich in nickel. The agitation is carried out by the use of an electrically driven small pump which forces air into the plating solution causing the latter to be in constant movement.

Solid Impurities are Removed by Filtration.

One result of the agitation is to disturb any solid impurities, dirt, etc., which may have fallen to the bottom of the solution and bring these in contact with the cathode surface. If they were not removed, they would cause serious trouble, since any particles which had deposited on the cathode would result in the formation of pits locally. They are, therefore, removed continuously by filtration, an automatic filter being attached to the plating tank, and the electrolyte pumped through a canvas filter-head back into the tank during the whole of the plating period.

Advantages of Automatic Nickel Plating.

Automatic nickel plating, which is widely carried out to-day as a basis for chromium plating, enables the parts to be plated to be chemically cleaned, washed in running water, nickel-plated, washed again in a number of "swills" and finally dried, without the necessity of handling the articles between each step in the process. This is effected by means of tanks fitted with "conveyor" equipment, the articles on suitable racks being lifted from one tank to the next mechanically and the whole series of operations being timed to a nicety. Many of the articles which are in common use are plated in this manner and some of the plating plants which produce them are illustrated in this article.

THE PRODUCTION OF LIME

By JAMES WATSON, D.Sc., F.I.C.

LIMESTONE may be considered as one of our important raw materials as it is utilised in so many of our principal industries to a very large extent. In the iron and steel industry, for example, for one ton of pig iron produced, about half a ton of limestone is required and a further 2 cwt. for converting the iron into steel.

Purity.

The purity of the limestone as a flux in the blast furnace is desirable and most of it has a magnesia content of less than 4 per cent., the stone being of a firm, close-grained structure and in size from 1 to 3 ins. As the function of the limestone is to unite with the siliceous material of the ironstone, it is therefore also desirable that the silica content should be under 3 per cent. and the alumina below 2 per cent., with the sulphur and phosphorus almost negligible and below 0.1 per cent.

Uses of Limestone—Paper Manufacture.

In the manufacture of paper large quantities of limestone are also utilised, each ton of sulphite pulp taking something of the order of 1 cwt. of lime, and in the manufacture of caustic soda, lime hydrate made from a high calcium limestone is made the causticising agent.

Calcium Carbide.

For calcium carbide, the production of which has now attained large dimensions as a source of supply for acetylene, there is used two tons of limestone to every ton of carbide produced, the purity of which must be verified by the chemist, as the phosphorus content must be lower than 0.01 per cent., and the magnesia less than 2.0 per cent. with the silica not exceeding 3.0 per cent.

Sugar, Glass, Chemical and Portland Cement and Paint Industries.

Sugar, glass, chemical and Portland cement industries are also some of the large users of limestone or lime as part of their processes. In the paint trade, it is

used considerably as a mineral filler, mostly in the form of whiting. This is the water-floated product obtained after grinding the limestone or chalk in wash mills, and allowing the finely ground material to run into settling backs or tanks, from which it is taken out after the excess of water has drained away, and dried on a kiln floor, then passed through a disintegrator and air separator to produce the finest qualities of gilders' whiting.

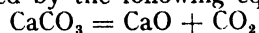
Distempers and Plastic Paints.

In the production of distempers and plastic paints it bulks very largely and putty is made by grinding together 85 per cent. of dried whiting and 15 per cent. of linseed oil in the pan mill, and there are innumerable materials produced from linoleum to rubber which contain this ground carbonate of lime or burnt lime as a mineral filler.

Agriculture, Textile and Building Industries.

But it is in the form of a quicklime or hydrate of lime that it enters more fully into active participation of industrial operations from agriculture to the textile industries and its extensive application in the building industry as a component of sand-lime bricks, and the making of lime mortar, so that the control of its production in the various types of kilns is of interest to the chemist.

Lime or quicklime (CaO) is more or less pure according to the quality of the limestone, chalk and other substances used in its manufacture and which are more or less wholly composed of carbonate of lime. During the burning in the kiln the carbonic acid gas is driven off as represented by the following equation:—



that is, if theoretically pure limestone were available then 100 parts would produce 56 parts of quicklime.

Analyses of Typical Varieties of Lime.

In practice this is not attained as will be seen from the following analyses of

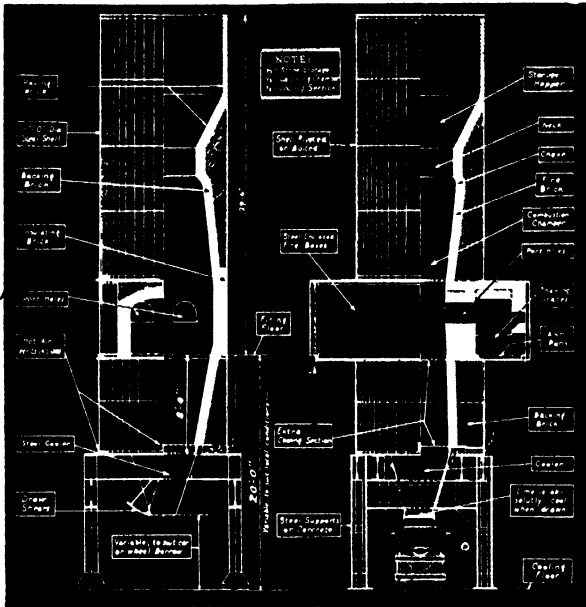


Fig 1 —CROSS SECTION OF A COAL-FIRED LIME KILN

typical varieties of lime made in this country

		White Lime Per cent	Grey Stone Lime Per cent.	Hydraulic Lime Per cent
Silica		1.50	10.40	16.95
Oxide	dumina	0.75	4.85	9.88
Lime		91.72	80.74	66.14
Magnesia		1.55	0.45	1.25
Alkalies		0.75	1.50	0.12
Loss on ignition		3.73	2.06	5.46
		100.00	100.00	100.00

Kilns Used for the Production of Lime.

The chief types of kilns used for the production of lime are draw kilns, shaft kilns and flare kilns.

Draw Kilns.

This type of kiln is of the inverted cone shape which at its base has a diameter of 5 ft. 6 in. and tapering outwards and upwards until it is from 9 to 13 ft. in diameter at the top.

A kiln of this type is usually erected so that it can be filled economically from the top, the pieces ranging from 4 in. to 6 in. in size, which are tipped into the kiln with alternate layers of fuel, usually anthracite culm and coke, the culm giving 10,000 to 11,000 B.T.U. per lb.

About 3 cwt. is burnt for each ton of lime produced, the lumps being piled above the top of the kiln in the form of a cone, to allow for the fall of the material

during burning. Generally this type of kiln is open to the weather and only protected from strong winds by a movable screen.

When quite burnt through, which is indicated by the level of the top layer, and the absence of flame or gases evolved, and thus takes about five days for a 24-ton kiln, then the lime is allowed to cool, the furnace bars at the base of the kiln are removed and the contents of the kiln fall into the drawhole and removed in trucks to the store or grinding shed.

Flare Kilns.

These are most useful, in that the products of combustion of the fuel, such as ash, etc., do not contaminate the lime in the kiln, and a much better colour is thus obtained with the lime as only the flame from the furnace reaches the stone with the

exception of that from the slight amount of fuel loaded into the kiln between the layers of stone.

The stone, whether "greystone" or "white chalk," is usually blasted in the quarry by means of black powder which causes the stone to be dislodged with the smallest percentage of fires, and manual labour with pick and crowbar readily breaks up the loosened face of rock. The best selected stone only is sent to the kiln and in size not exceeding 6 in.

The kiln is some 16 ft. in diameter and 20 ft. high and is built of good stock bricks with the exception of the furnace section, which is of firebrick. There are two and often three furnaces, running from front to back of the kiln, and during loading some larger 9-in. lumps of chalk or limestone are built in the form of arches over each furnace area. The space between the arches is filled in with the smaller lumps but none is less than 2 in. in size.

The kiln is loaded to the base of the brick dome over the kiln and this has a short vent shaft to allow the gases to escape. After the kiln is loaded the openings are closed with bricks, which are luted over, and fires are started on the furnace grates.

Fires Should be Started Slowly.

As the stone is generally damp and often somewhat soft it is usual to start the fires slowly, so that the moisture may be driven off gradually, otherwise cracking and breaking away of the stone takes place, blocking the draught.

One of these flare kilns will usually produce from 40 to 50 tons of lime per burning, and take about three days to burn through and cool off, but smaller ones are in operation in many places. At one works the output from the kiln is from 18 to 20 tons per week of well-burnt white lime, and whilst 1 ton of broken steam coal is spread through the somewhat hard stone in the kiln, 5 tons of coal mixed with three tons of coke are used in the two furnaces. The amount of fuel used is on the high side but as the lime was to be used in the manufacture of sandlime bricks, it was felt that a little extra fuel used would ensure complete burning; a better ratio would have been $6\frac{1}{2}$ cwt. of coal to 1 ton of lime produced.

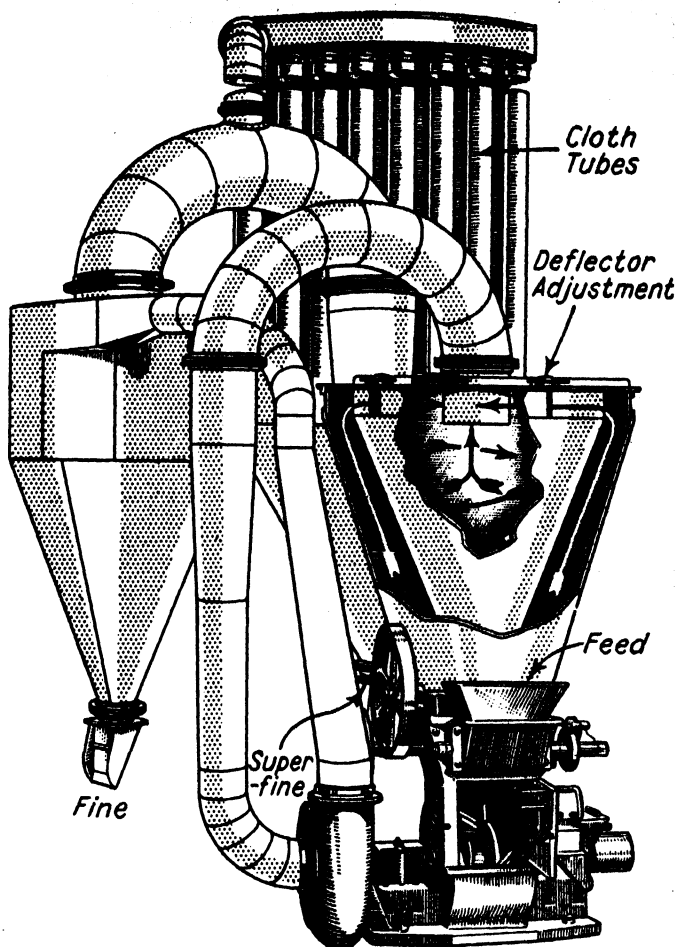


Fig. 2.—A RAYMOND PULVERISER WITH AIR SEPARATOR, CYCLONE COLLECTOR AND TUBULAR DUST COLLECTOR.

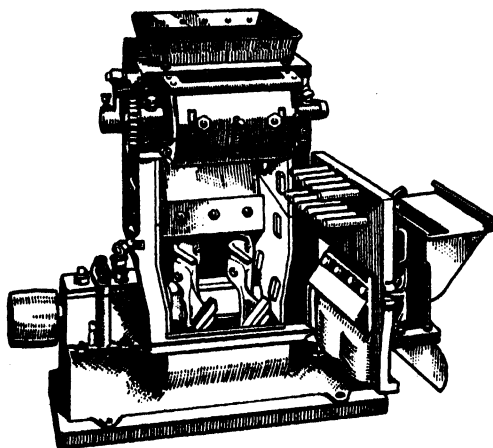


Fig. 3.—THE THROW-OUT ARRANGEMENT OF THE PULVERISER SHOWN IN DETAIL.

Continuous Shaft Kilns.

Of these there are numerous modifications which mostly resolve themselves into different designs of the burning zones, also charging and discharging gear, but the principle remains much the same in each type.

The main difference to be noted from the draw or flare kilns is the adaptation of mechanical devices for dealing with the materials, and by means of forced or induced draught or both, the burning can be kept more under control so as to produce uniformity of quality with minimum fuel requirement.

The kiln consists principally of a vertical shaft of varying height and diameter to suit the required output per day. A 50-ft. high by 10 to 12 ft. diameter is a usual

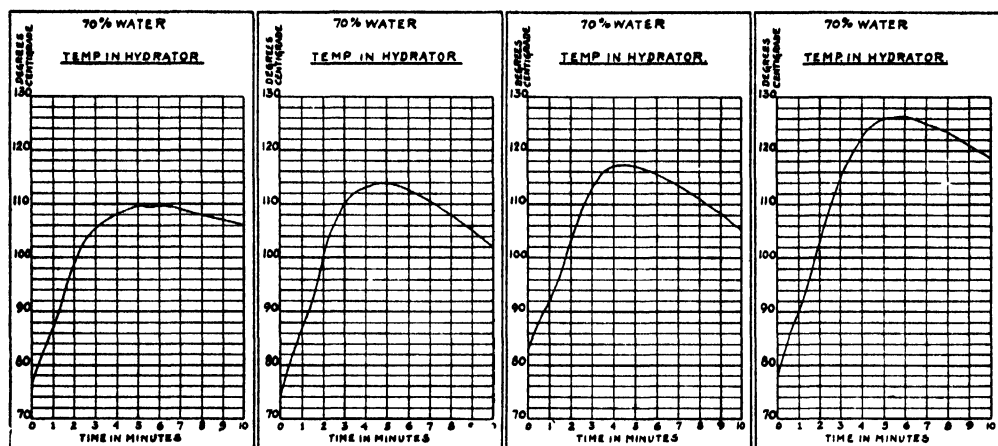


Fig. 4 —TIME-TEMPERATURE RECORD OF FOUR SUCCESSIVE BATCHES IN A LIME HYDRATOR

size. The shaft is built of brickwork-firebrick inside, then an insulating layer of heat-resisting material such as kieselguhr, then ordinary brickwork banded at intervals with strong iron hoops and often covered with a steel casing so as to prevent any air passing through cracks which may develop in the brickwork.

The limestone and fuel are brought to the kilns by overhead runways and fed in continuously from the hoppers which are fitted with automatic delivery and measuring apparatus, so that after the batch is fed in, the aperture is automatically closed to prevent admission of air to the kiln.

White Lime.

Where it is desired to produce the white lime free from even the contamination of the light grey ash of the coke, then the heat is obtained from the burning of coal or coke in separate furnaces built against the side of the main shaft of the kiln. The use of producer gas or oil is only resorted to in exceptional cases and only where these are to be got more readily and cheaply than coal and coke.

If the fuel is to be fed in with the limestone, then only small coal with a slight amount of coke added need be used, and it is possible to obtain an efficiency ratio of $6\frac{1}{2}$ tons of lime per ton of fuel used, about twice the efficiency of the older types of kiln.

There is more skilled attention required to operate this type with constant supervision by the chemist to see that the burning zone is kept constant at the same

height in the kiln. Theoretically 1 lb. of pure carbon burning to carbon dioxide should produce 12.52 lb. of gas and give a temperature of 4800° F., but coal is not pure carbon and the gases evolved are mainly methane, hydrogen and carbon monoxide, which constitute the volatile constituents of the coal (30 to 35 per cent.).

Temperature Required in Kiln.

The temperature required in the kiln for decomposition of the limestone into lime and carbonic acid gas is 1600° F. and it takes 619 B.T.U. to heat 1 lb. of limestone to this temperature and 1,378 B.T.U. to decompose it, or it may be expressed thus:—

Of every 1,000 units of heat supplied by the coal 195 units are required to preheat the limestone, 665 units to produce decomposition and 140 units are lost through the waste gases and in the hot lime discharged, which has a specific heat of 0.22.

Hydration of the Lime.

There are about as many methods of converting the lime into hydrate of lime as there are for producing the lime from the natural quarried limestone or chalk. Hydrate of lime is a chemical compound containing 75.7 per cent. of lime (CaO), and 24.3 per cent. of water and is of the nature of a dry powder having a specific gravity of 2.34, whereas that of lime is 3.18, so that expansion of volume takes place during the process of hydration to the extent of about 80 per cent.

The lime from the kiln is sorted and any overburnt or underburnt removed, then it is passed through crusher rolls and ground to $\frac{1}{4}$ in. and less and is automatically weighed into the hydrator.

This may either be one of the continuous or batch types. Of the continuous hydrators there are many types both vertical and horizontal.

Vertical Type Hydrator.

In the vertical the crushed quicklime is elevated to a weighing machine which automatically delivers it on to the first tray of the hydrator. The amount of water necessary is also added at the same time, and as the centre vertical shaft rotates, the blades or tynes on the radial arms keep the lime in motion, turn it over and so prevent any local overheating of the particles.

The water when it meets the surface of a lump of lime starts a violent reaction, and so much heat is evolved that the particles of lime which have become hydrated may be decomposed and hard yellowish particles formed, as the temperature may rise to over 700° F. These particles act like overburnt lime and take some time to hydrate, causing later expansion.

For this reason, the lime whilst being hydrated must always be kept on the move, and in this vertical type of plant, after passing round the top tray, which is about 4 ft. 6 in. in diameter, it is shot down to the second tray and the same mixing takes place until it reaches the last tray, of which there are usually eight. The capacity of such a machine depends on its internal volume; with 1,400 cubic ft. capacity the output would be 15 tons per hour with a power consumption of 8 h.p.

Horizontal Type Hydrator.

This is a long cylindrical drum about 3 ft. 6 in. in diameter and 20 ft. long, fitted with lifters. The crushed lime is fed in, sprayed with water and by the rotation of the drum the lime and water are intimately mixed and dry hydrate of lime delivered at the outlet end.

Batch Hydrator.

This is considered as being the simplest in operation, as it is not possible always to guarantee the quality of the lime being

the same each day, so this machine enables continuous inspection and sampling to be carried out whilst the machine is in work, and the chemist is enabled to give a longer or shorter time for hydration according to the results of his tests.

A machine of this type consists of a large steel trough 10 to 15 ft. in length and 18 in. in width according to the capacity of the machine. Through the trough passes a steel shaft fitted with sets of paddle blades, which ensure that every portion of lime is thoroughly mixed with water and turned over at least twelve times per minute. The whole trough is built in with a vertical steel casing fitted with vent pipe, inspection door and outlet, and capable of hydrating up to 20 cwt. of lime per hour.

The machine takes about one minute to charge with the lime and the stirrers are at once set in motion, whilst the requisite amount of water is added by means of a spray extending the length of the trough.

The amount of water is slightly in excess of theoretical requirements, as the heat developed vaporises some of it.

But in whichever way this lime is hydrated, it is the usual practice to store the lime hydrate warm from the hydrator, so as to mature it, as there may be small particles of the oxyhydrate still present, and even after storage it is good practice to pass all the hydrate through an air separator afterwards. The value of the chemist's work in checking the quality of the lime and lime hydrate produced, and seeing that they meet the necessary requirements, is fully appreciated by the improvement made in these materials and the retention of the confidence in them by the large buyers.

Samples of limestone and fuel, both coal and coke, are being tested at regular intervals by the chemist. Then he has the sampling and testing of the quicklime at regular intervals as the limestone may vary in different strata; each consignment of fuel changes in heating value, the draught in the kiln may vary, or the calcination of the limestone may result in under or overburnt product.

Then there are the analyses of the exit gases from the kiln to be carried out, so that he may make any necessary adjustments in the fuel or air supplied to effect economy of production.

PAINTS AND VARNISHES

PART V.—WATER PAINTS AND DISTEMPERS

By H. COURTNEY BRYSON

IT has become the custom in the trade to apply the term distemper to a paint produced solely by the aid of a water-soluble binding agent, while the term water paint is reserved for those materials which contain oil, being made on an emulsion basis. Distempers are used chiefly for producing ceiling whites or for cheap wall finishes. They are often so lightly bound that they readily rub off either in the wet or the dry condition.

Formula for Typical Distemper.

A typical distemper consists of —

Glue (rabbit skin), 7 lbs

Water, 12 gallons

Pigment, chiefly chalk, 2 cwt

Mirbane oil (as preservative) $\frac{1}{4}$ pint.

Powdered Distemper.

Powdered distemper commonly consists of powdered glue mixed with the appropriate pigments. The best powdered distempers, however, are made from

casein, and consist of five principles :

- (1) The binding agent—casein,
- (2) The alkali-proof pigment ;
- (3) The vehicle—water ;
- (4) A basic salt—to dissolve the casein ;
- (5) The insolubilising agent.

The functions of (4) and (5) are often combined in a single substance, e.g., lime.

Casein Suitable for Cold Water Paint Manufacture.

A specification for a casein suitable for the manufacture of cold water paint is given below —

Moisture, not over 9 per cent., on oven-drying at 105°C.

Fat, not over 1 per cent., on extraction in a Soxhlet.

Ash, not over 4 per cent., on ignition in a crucible.

Odour, sweet.

Completely soluble in 15 per cent. of borax (but see Mummery and Bishop's test under "Leather Finishes").

Ground to at least 90 mesh.

It is interesting to note that the viscosity of any given

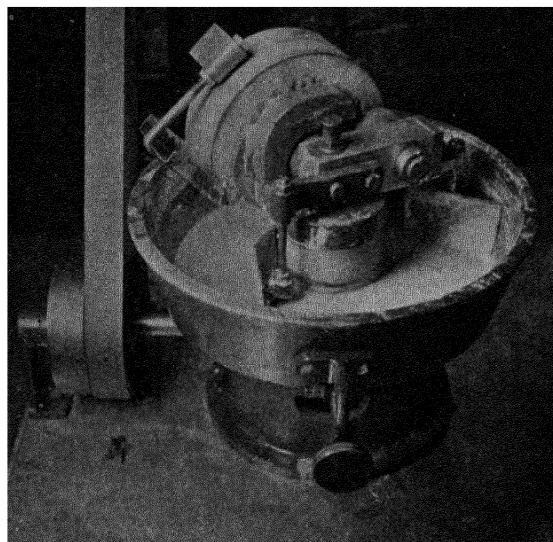


Fig. 1.—EXPERIMENTAL EDGE RUNNER MILL AS USED FOR THE MANUFACTURE OF DISTEMPERS

The wheel-like stone runs round the trough containing the distemper medium and the pigment. A blade (shown on the right inside the trough) turns over the mass and facilitates mixing. A knife removes adhering material from the stone runner. The pressure on the mass is adjusted by altering the height of the trough.

casein in solution varies directly as the ash content, in other words with a given amount of water caseins such as rennet produce a more viscous solution than caseins such as self-soured lactic with less than half the ash content of rennet.

Lactic casein is usually employed for the manufacture of casein paints, because of its suitable viscosity and stability, but if the properties of rennet casein were more thoroughly studied in this connection or if sulphuric acid casein were readily obtainable on the European market, it is probable that these would find a much wider use in paint and distemper manufacture.

Rennet casein, though not dissolved by the same range of solvents as lactic casein, can be made up into paints with great resistance to water and abrasion. Unfortunately, its viscosity is high and it is very sensitive to small changes in the constitution of the solvent. For example, the addition of red oxide is often sufficient to precipitate calcium paracaseinate (rennet casein) from solution. The ordinary ammonium and sodium caseinates are much more stable.

A plain film of any casein salt on exposure to light and air gradually becomes insoluble with passage of time. If certain insolubilising agents are present such as formaldehyde, lime or potassium bichromate, insolubility is conferred immediately.

Lime.

Calcium hydroxide not only acts as an insolubilising agent, but is also a solvent for casein and for this reason is usually used in the manufacture of cold water paints. It performs a triple function. When water is added to a mixture of lime and casein, a part of the lime dissolves in the water and then reacts with the casein to form calcium caseinate, more lime then dissolves and reacts till the whole of the casein has been converted. Though lime is more soluble in cold than in hot water, it is better in very cold weather to add warm water to the mixture or the formation of the caseinate is slow. On no account should the mixture be warmed or the mass will set to a strong irreversible gel.

The quality of the lime employed is extremely important. The amount of active CaO should be determined in each batch by the sucrose method. Titration

with hydrochloric acid and phenol-phthalein sometimes recommended is unsatisfactory. The anomalies of lime are well known in practice, but little investigatory work appears to have been done. It is a very complex substance and is susceptible to profound modifications on prolonged storage as the Old Masters knew well.

The pigment can perform a variety of functions. It may act as a hiding agent, a thickening agent, a colouring agent or it may assist in the spreading of the paint under the brush or in keeping other pigments in suspension. The nature of the medium as well as the nature of the pigment determines which of these functions the latter will fulfil.

For example, in media with different refractive indices the same pigment will vary in its capacity for obscuring the surface to which it is applied, since hiding power is determined by the intensity of the reflection of light at the pigment/medium interface. Chalk is the chief pigment used in connection with casein for paint manufacture.

It is cheap and plentiful, it does not flocculate readily in alkaline media, it can be easily tinted and its refractive index is sufficiently different from the dried medium to render it fairly opaque. It is essential that the amorphous chalk whiting composed of the skeletons of marine organisms be employed and not the precipitated chalk which has a crystalline structure and consequently gives a film with poor hiding power and low strength.

Paris white is the finest variety of chalk whiting and it should be ground to such a degree that not more than .5 per cent. is left on a 300-mesh sieve. A certain percentage of clay or asbestine is also usually added in order to assist the suspension and improve the brushing qualities.

Other alkali-proof colours used with casein are red oxides, umbers, ochres, chrome yellow, chromium oxide green, ultramarine and carbon black. Titanium oxide, zinc oxide and lithopone are used in the manufacture of oil-bound distempers but not in the ordinary variety. In the presence of zinc oxide casein solutions suffer a rapid drop in viscosity with passage of time.

Flocculation.

The greatest difficulty in the manufacture of all water paints is due to the

interfacial surface relation of the medium and the pigment which in turn is influenced by the relative pH values. In media with a pH value above eight, many oxides show a great tendency to flocculate. This flocculation of the pigment has many serious consequences, which have been mentioned under Paints.

Proportions.

The ratio of the constituents of the paint has a great influence on its life and working properties. It is obviously essential that there should be sufficient alkali present to dissolve all the casein, though complete solution may require some 15 minutes after the addition of the water. If insufficient lime is present (under 25 per cent.) the casein will not dissolve readily and a chalky paint film, poor in adhesion, will result; while excess will tend to precipitate the casein and give poor working qualities. M. Swartz states that, using sulphuric acid casein and a high-grade lime, 100 parts of casein require 119 parts of $\text{Ca}(\text{OH})_2$.

The proportion of pigment is also an important matter. Deficiency leads to poor hiding power and a tendency to crack and peel off. The correct proportion has to be determined separately for each pigment. The easiest way of estimating this is to apply a definite series, containing predetermined variations of pigment, to pieces of smooth writing paper. If on drying there is a tendency to curl (due to contraction of the casein) the binder is in excess, while flaking denotes too great a proportion of pigment. The best ratio is usually in the neighbourhood of four to six times the amount of binder. A typical formula giving excellent results is as follows:—

Casein = 10 ;

Lime = 10 ;

Chalk = 60 ;

Pigment (lime proof) = 20.

Testing and Weathering.

Tests for specific gravity, settling properties, hiding power, covering power, washability and durability are essential for the full description of a good water paint.

Specific gravity is determined in the normal way, settling by making up to correct consistency, pouring into a graduated tube and observing the degree of settle after, say, 24 hours.

Washability is estimated empirically by exposing the film to light and air for a week, soaking in water for 12 hours and then rubbing with a tooth brush of standard stiffness. The test is made more stringent by using a saturated solution of borax instead of water and by brushing with an abrasive. Accelerated weathering tests as already explained can be performed to determine the relative durability, but the true durability is estimated by exposing test pieces on wood, metal and slate at an angle of 45° facing south. This represents in England the maximum (i.e., worst possible conditions).

It is well known that the three summer months are the most destructive to paint and cellulose films on account of the disintegrating influence of ultra-violet light. Casein films are opaque to all violet radiation and consequently the severest conditions are presented by wet and abrasion. It is interesting to note in this connection that many specimens which fail badly under the washing test stand up well to weathering.

Oil Bound Distempers.

These are made by incorporating a certain proportion of oil into an aqueous base composed of casein or glue. An excellent formula originated by the writer, and which has been extensively quoted, consists of:—

(1)	Casein	..	..	30 kilos.
	Water	..	..	150 litres.
	Borax	..	..	3.5 kilos.
	Phenol	..	..	1.0 kilo.
(2)	Formaldehyde	..	..	2.0 litres.
	Water	..	..	5.0 litres.
(3)	Pale boiled oil	..	..	.15 kilo.
	White Spirit	..	..	10 litres.
	Rosin	..	..	15 kilos.

Soak the casein in the warm water, add the borax, then the phenol. Allow to stand for 24 hours. Then add (2) slowly with constant stirring. Dissolve the rosin in the hot oil and add in a slow stream to the hot casein, beating up in an electric whisk. Grind in the colours to the desired tint.

If trouble is experienced with flocculation of certain pigments the pH value may be adjusted by increasing the amount of borax.

The usual tests applied to oil-bound distempers are essentially practical ones designed to answer the following questions:—

Does it brush out evenly and well?

Are the brushes hard to clean after use?

Does it dry "sheary," i.e., streakily?

Is the hiding power as well as the adhesion good?

Does it rub off readily in the dry or in the wet?

Is it stable on storage and during transport?

ANALYSIS OF DISTEMPERS AND WATER PAINTS.

Determination of Oil Content.

Water paints contain, as already indicated, an inorganic pigment bound with an aqueous solution of an albuminous body together with oil in emulsion plus possibly some gum or resin.

The Pigment.

This is generally lithopone with a little china clay or chalk or more rarely calcium sulphate. The colouring matter is either an earth colour or an alkali-proof lake. The identification of the former portion is carried out by the usual routine method. Similarly earth pigments are fairly easily identified, but if it be desired to recognise with certainty the lake pigment (which is rarely the case) then a lengthy process must be adopted for details of which a standard book on the subject must be consulted.

Amount of Rosin Present.

If the distemper is in paste form it must be dried. The pulverised residue is then extracted with ether. On evaporation the oil is left and its weight may be calculated as a percentage of the original. Rosin may be present and may be identified by the Liebermann Storch reaction. An examination of the film from the ether solution gives a valuable guide to an experienced person of the amount of rosin present.

Estimation of Soap.

Soap which is often present as an emulsifying agent or lime soaps which are sometimes used for hardening albumins may be estimated by further extracting the ether-extracted residue with hot alcohol. The residue from this alcohol treatment is divided and part is examined, acidified with hydrochloric acid and then extracted with ether to remove fatty acids due to lime soaps.

The remainder of the residue is dissolved in water, aided if necessary, with a few drops of ammonia. Insoluble matter is allowed to settle from the dilute solution and the supernatant liquor decanted. The albuminous matter is then thrown down with hydrochloric acid.

Nature of the Precipitate.

The nature of the precipitate is readily recognised by the experienced. Glue gives a more slimy deposit than casein, which produces firmer curds of a more flakey nature. An indication, too, is obtained from the original paste distemper, which if alkaline suggests the presence of casein while neutrality indicates glue.

In either case, a nitrogen determination by the Kjeldahl method is performed on the original distemper and this percentage multiplied by 6.39 or 5.55 gives the percentage of casein or glue respectively in the sample.

If both bodies be present, the steps necessary for their separation are so tedious as scarcely to be worth while. Dextrine is sometimes used as a binding agent and may be recognised by boiling a little of the original paste with distilled water, cooling and adding a few drops of very dilute iodine solution. Dextrine is indicated by the formation of a brown coloration.

BACTERIOLOGICAL EXAMINATION OF WATER

PART II.—ROUTINE METHODS OF EXAMINATION

By H. F. FERMOR, F.I.C.

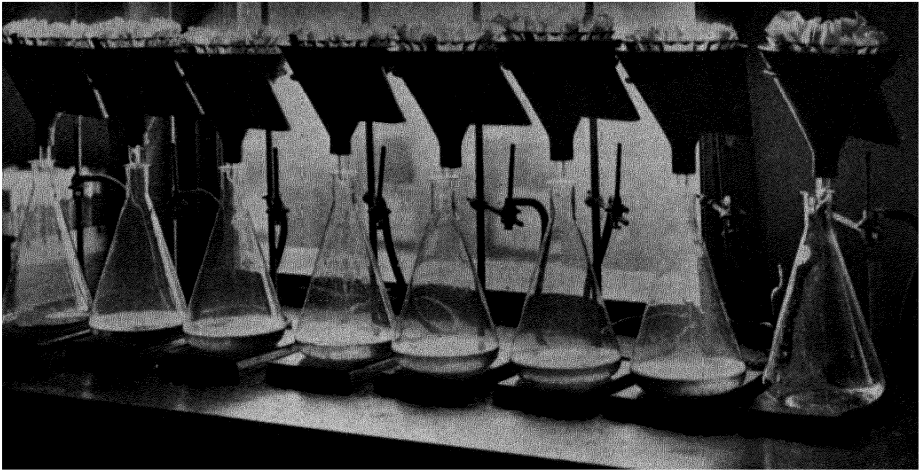


Fig 1—THE PREPARATION OF THE AGAR-AGAR.

When mixed with water it forms a jelly to which can be added various reagents to be used by the microbes as food

FROM the point of view of a water bacteriologist there are three categories of microbes. Those normally present in water and harmless, those typically present in sewage and which, if found in potable water supplies are taken to indicate contamination, possibly of recent date; and last of all, those organisms which are definitely pathogenic to man. For these a special search must be made, but the chances are very much against the bacteriologist finding any. He usually gets his information very late and after pollution has taken place. Then the harmful germs are by no means so healthy as the comparatively harmless ones, consequently they tend to die quickly as they have a decided dislike to fresh air and sunshine.

Only 23 Micro-organisms are Definitely Pathogenic.

It is very unlikely that a water will be free from micro-organisms, and it is comforting to know that out of 195 sorts isolated from water only 23 were proved to be definitely pathogenic, and many of these, while giving rise to disagreeable symptoms, were not as a rule fatal.

Some of the harmless microbes found in water are very pretty to look upon for they are brilliantly coloured. As Koch first found out, these are best grown on pieces of sterile potato. He saw some coloured spots on a piece of neglected potato, studied them under the microscope and thus added a new method of bacteriological technique.

B. Prodigiosus.

A common red microbe is *B. prodigiosus*, so named in 1886 but known since 1823 as a living thing, and used hundreds of years before in attempts to produce miracles, for it grows readily on bread and other starchy materials exposed in damp situations. It is always of a red colour and very frequently resembles blood. This microbe has a characteristic smell, which is due to the production of trimethylamine.

B. Violaceus Berolinensis.

Another microbe, interesting to Londoners as it has been found in the River Thames, is *B. violaceus berolinensis*. It is of a deep violet colour, forms spores, and reduces nitrates to nitrites.

In fresh water there are sufficiently numerous coloured bacteria to enable an artist to grow a picture if he were so disposed.

Sea Bacteria.

As might be expected, the sea also contains bacteria, and a good many of them are luminous; hence a fish is seen to be phosphorescent in the dark, sometimes when it has undergone the process of curing, as in the case of haddocks. In some cases sufficient actinic light is emitted that photographs of objects, such as skulls, can be taken.

Microbes in Sewage.

There are many more sorts of microbes in sewage than in water used for domestic purposes. Some of these are like criminals in a civilised society. It is impossible to keep them out but it is at least desirable for the police to know them. The bacteriologist is in this case a sort of policeman for hygienic purposes.

Sewage Organisms.

The fauna and flora of a potable water is usually harmless, but suspicious microbes may be found amongst them. These as a class can be termed sewage organisms. Some are more dangerous than others but all are undesirable, so the bacteriologist has selected one which is comparatively easy of detection and uses it as what might be termed "an indicator micro-organism" of probable pollution. This is the *B. coli* communis.

The sewage is a complex mixture of many sorts of microbes, the

number growing on nutrient agar at 37° being estimated as more than one but less than ten millions in one ml. Of these 100,000 are *B. coli* communis, 1,000 streptococci, and about the same number of spores of *B. enteritidis sporogenes* are present.

The water bacteriologist wants to know in the course of his investigations the number of microbes in a unit volume of water, if any of these are harmful and, if so, how they can best be rendered harmless.

The Medium—Agar-Agar.

The medium generally used for the cultivation of bacteria is agar-agar. When mixed with water it forms a jelly to which can be added various reagents to be used by the microbes as food. At a temperature of 37° it is a solid, and this degree of heat is very suitable for the growth of *B. coli* and similar organisms.

How Agar-Agar is Used.

The agar-agar is used as follows in the examination of a sample of water. A quantity of water, say 10 ml., is placed in a Petri dish, and about 40 ml. of liquefied nutrient agar added to it. The water and agar is then mixed by gently shaking the dish and the result is that the mixture speedily solidifies. The dish is then inverted, a space being left between the two parts by the insertion of a bent paper-clip, in order to enable the condensation water formed when the dish is placed in the incubator to escape and so prevent the formation of "skaters" on the surface of the agar.

The dish and its contents are then incubated at a temperature of 37° for from 24 to 48 hours, at the end of which period of time the number of micro-organisms which have grown on the agar is counted and this is regarded as an index of undesirable contamination in the original sample.

The Result Obtained is only Relative.

While the tests with agar plates give an idea as to the number of organisms present which grow at temperatures of 22° and 37° respectively, the result is only relative, for obviously all the microbes present are not counted as there is a time limit to the experiment. For most purposes the tests are sufficient but, if desired, the agar could be mixed with

various sugars and other substances used as indicators so as to make the experiment a differential one

Testing for the Presence of Certain Types of Microbes.

The next procedure is to test the sample of water for the presence of certain types of microbes which are known to be constantly present in sewage as well as in the intestinal tract of man. Such an organism is the *bacillus coli communis* (*B. coli*), which if not dangerous itself is usually associated with undesirable companions.

How *B. Coli* is Treated.

In dealing with such organisms, the bacteriologist either tries to encourage their growth, or to kill them. In the first case he gives them food on which they, as a class, can readily thrive and consequently grow quickly. In this way is *B. coli* treated.

Clostridium Welchii.

There is another sort of organism known as *Clostridium welchii*, which can produce spores as well as multiply by division. These spores can stand a higher temperature than the microbe itself. Consequently, on heating a liquid containing the organism to 80° for ten minutes the spores only survive. The spores are fed on milk tinted with litmus. The so-called "stormy fermentation" is produced in the tube after it has been incubated at 37° for from 24 to 72 hours and the litmus is turned red, showing the presence of an acid, which also has a characteristic smell.

MacConkey's Medium for *B. Coli*.

In the case of the *B. Coli* the microbes are encouraged to multiply by growing them in MacConkey's medium, which consists of a solution of lactose, peptone, sodium chloride and sodium taurocholate coloured with litmus. In the preliminary tests for this organism it is convenient to use a liquid medium and add measured quantities of the sample of water to test tubes containing the medium arranged in a rack.

The sample of water is distributed as follows —

100 ml. is added to a tube containing 25 ml. of MacConkey medium of quintuple strength

10 ml. into each of two tubes, one containing 10 ml. of peptone water (1 per cent. peptone), the other 10 ml. of double strength MacConkey medium.

1 ml. into a tube containing 10 ml. of single strength MacConkey medium

0.1 ml. into a tube containing 10 ml. of single strength MacConkey medium.

In the rack also is a tube containing a measured quantity of water, 9 ml., with sufficient fluorescein to give it a green colour so that 1 ml. of the solution, after the

addition of 1 ml. of the water sample, will contain 0.1 ml. of the original sample.

Different Colours Indicate the Amount of Water in Each Tube.

The amount of water to be placed in each tube is indicated by the colour the label on the tube on which is the identification number. The colour of the wool with which the tubes are is a guide to the medium contain-

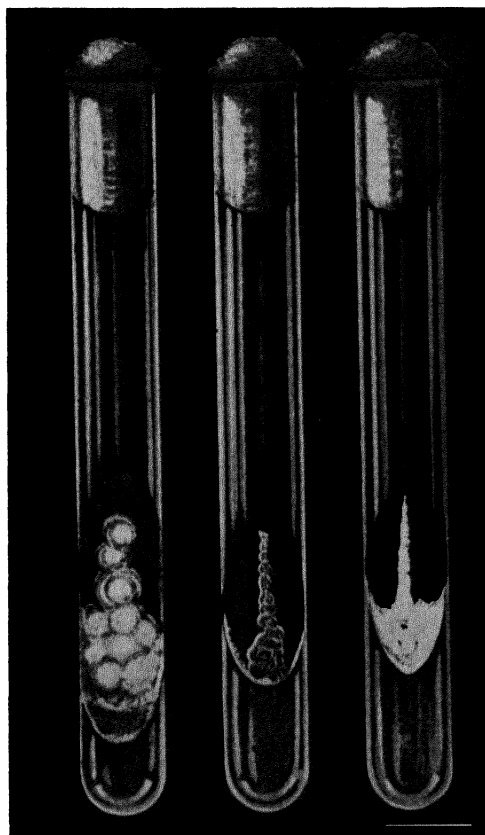


Fig 2 — CULTIVATIONS ON AGAR SLOPES
From left to right: *bacillus anthracis* (anthrax), *bacillus subtilis*, *staphylococcus cereus albus*.



Fig. 3.—RACK ARRANGED FOR THE PRESUMPTIVE TEST OF A SAMPLE OF FILTERED WATER FOR *B. COLI*.

tubes, while on each label is printed the amount of the original sample of water placed in the tube and, as an additional safeguard, the colour of the label indicates the amount of the water sample placed in the tube.

The Tubes are now Heated and Placed in an Incubator.

The tubes having had the appropriate amount of water put in them, are then placed in a water bath heated to a temperature of 37° for about an hour, after which they are transferred to an incubator at 37° and allowed to remain there for about 24 hours, at the end of which time they are examined.

Examining the Tubes for Coli-like Organisms.

If the original sample contained any coli-like organisms then the contents of the tube will have a red colour, indicating the presence of an acid, produced by the fermentation of a sugar, lactose, which has turned the blue litmus red. The small inner tube, instead of being at the bottom of the larger one, will be seen to be floating near the top of the liquid and will contain a variable amount of gas consisting principally of a mixture of carbon dioxide and hydrogen, the ratio of these gases present giving in many cases an idea as to the sort of organism present.

Testing for the Presence of Indole.

The tubes giving positive reactions are reserved for further examination. The tube containing peptone water is tested for the presence of indole by noting if it gives a red coloration with Ehrlich's reagent (an acid solution of paradi-methylamidobenzaldehyde in alcohol). Should such be the case, then it is advisable to question provisionally the quality of that sample of water—more particularly if it also gives a positive result in the 10 ml. MacConkey tube.

This change of colour in the medium from blue to red and the presence of gas in the inner tube are regarded as presumptive evidence as to the presence of coli-like organisms in the original sample of water. This necessarily requires confirmation, and in order to do this it is more convenient to employ tests in which solid media are used.

In this case agar is useful. It is mixed with food material for the benefit of the microbes, and, in addition, is coloured with a dye, say neutral red, for the benefit of the bacteriologist.

Confirmatory Test for Coli-like Organisms.

Two agar slopes or slants are used. One is contained in a test tube plugged with white cotton wool. The medium therein contains lactose or milk sugar. The other

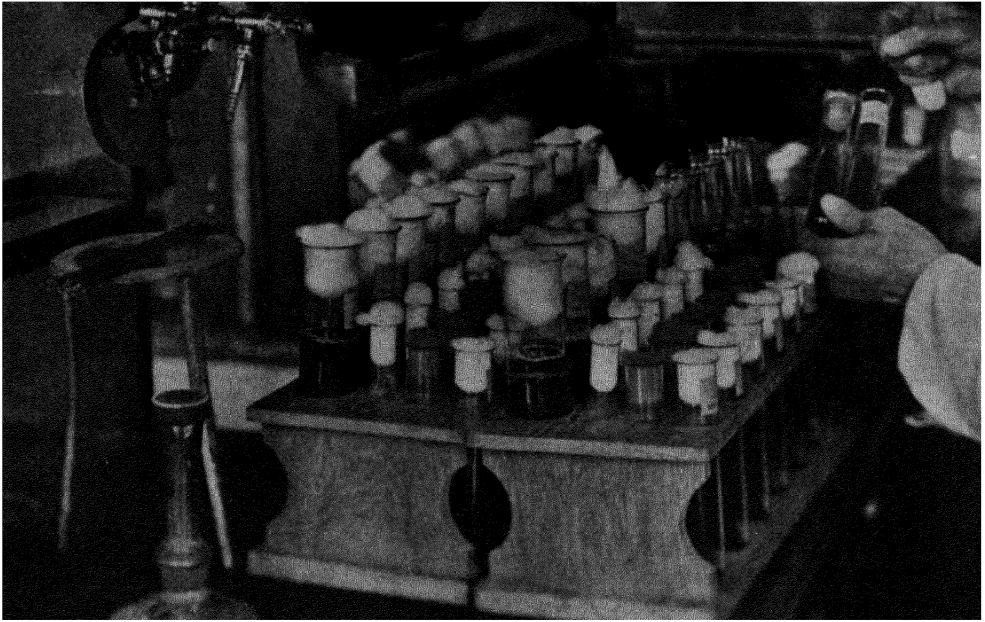


Fig. 4 —CONFIRMATORY TEST FOR PRESENCE OF COLI-LIKE ORGANISMS

The rack is arranged for testing the positive "presumptive" test results by growing some of the micro-organisms on agar-lactose and agar-saccharose slopes

tube has a slope of which cane sugar or saccharose is a constituent, and this tube is plugged with red cotton wool.

The Tubes Required for the Test.

The test is conducted as follows :—

In a suitable rack are placed in order, beginning at the back, the positive MacConkey tube, a tube containing an indefinite quantity of sterile water for dilution purposes, a tube plugged with red wool which contains an agar-saccharose slope, and in front of all, a tube plugged with white wool and which contains an agar-lactose slope

Transferring the Inoculated Water to the Agar Slopes.

A sterile iron wire, instead of the usual one of platinum, with one end bent into a small circle, is used to take a sample of the liquid from the positive MacConkey tube and is transferred to the tube containing the sterile water. The wire is moved about until the contents of the loop are fairly evenly distributed. A loopful of the inoculated water is then taken from the dilution tube and spread over the surface of the agar-saccharose slope. Then the agar-lactose slope is treated in the same way.

Next Heat and Examine.

The inoculated tubes are then placed in an incubator at a temperature of 37° and at the expiration of 24 hours their condition is examined. It will usually be found that red colonies have grown on the lactose-agar slope, while, if the organisms are typical coli, the agar-saccharose slope will have white colonies on it. If such be the case then in all probability the original microbe was a coli-like organism. In this way the presumptive test is confirmed.

Anyone who has been introduced to the *B. coli* group of organisms will recognise that the presumptive and confirmatory tests as above outlined give a good deal of information, comforting or otherwise, but that on occasion it is advisable to examine the behaviour of the microbes more closely.

Closer Examination of Microbes.

In order to do this, advantage is taken of the fact that microbes are fond of sugars. At the same time some of them can utilise, and in so doing decompose, peptone and give rise to the formation of indole.

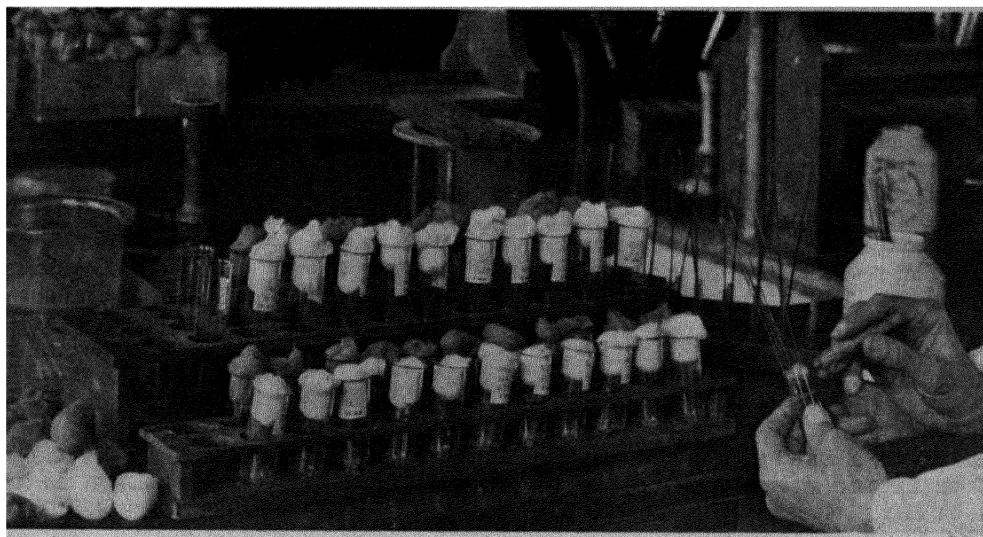


Fig. 5.—RACKS ARRANGED FOR TESTING THE COLI-LIKE ORGANISMS FROM THE CONFIRMATORY TEST IN ORDER TO ASCERTAIN THE BIOLOGICAL ATTRIBUTES OF THE COLI-LIKE ORGANISMS.

The sterilised iron wires on which the microbes are conveyed from the slopes to the tubes can be seen sticking out of the tubes. When there are two tubes containing a similar reagent, one is marked with a red bar by means of a grease pencil.

Reagents Required.

The procedure adopted is as follows : The various sugars used are incorporated in a gelatine medium, coloured for identification purposes with neutral red, litmus, etc. Other tubes are required which contain 1 per cent. peptone water and 0.5 per cent. solution of sodium chloride.

Arrangement of Tubes.

These reagents are contained in small glass tubes of which there are two sets. One set is placed in a larger tube, plugged with red cotton wool, the other set in a similar large tube plugged with white cotton wool. The first large tube now contains six smaller ones, in groups of two, containing respectively gelatine with lactose, glucose and saccharose coloured with litmus, uncoloured and neutral-red. The second large tube holds four small tubes in two groups, one group being filled with 1 per cent. peptone water, the other with drops of 0.5 per cent. salt solution.

Raw Materials for the Test.

The raw materials for this test are some of the colonies growing on the agar-lactose and agar-saccharose slopes. One colony is selected from each slope for a more detailed examination; what sort of colony depends very largely on the personality of the bacteriologist.

Carrying Out the Test.

First the two tubes containing 0.5 per cent. salt solution are placed in holes bored in a piece of wood and a little larger than the tubes. One of the tubes has a red line made on it with a grease pencil. This tube is destined to have a micro-organism from the agar-lactose slope placed in it; the other small tube will have a colony selected from the agar-saccharose slope placed in it.

The microbes are conveyed from the slopes to the tubes on the ends of straight iron wires about 15 cm. in length, which have been sterilised. The microbe from the lactose slope should be red in colour, that chosen from the saccharose slope colourless.

It may happen that neither slope will have typically coloured colonies on it. In such a case select the most likely colonies to put through the tests. These will probably turn out to be non-typical coli, or it may be they are not coli at all and so may fail to give any reactions in the small tubes containing the sugars or in the peptone water tubes.

The two small tubes in the stand now contain 0.5 per cent. salt solution, together with a selected microbe and an iron wire. To each tube can now be added as many sterile iron wires as there are tests to be performed—in this particular case four

reagents are used, so that there must be three additional wires added.

How Tubes Containing a Similar Reagent are Distinguished.

The next problem is to transfer some of the micro-organisms from what might now be termed the stock tubes to the tubes containing the reagents. First of all be it noted that there are two tubes containing a similar reagent, so in order to distinguish these one is marked with a red bar by means of a grease pencil.

Inoculating the Tubes.

When inoculating the tubes, a wire is taken from the stock tube and placed in the appropriate tube containing a reagent, one marked if taken from the marked stock tube which contains a microbe taken originally from the lactose slope.

All the tubes having been inoculated, those with the red wool plugs, which contain gelatine media, are placed in an incubator at a blood heat for two hours in order that their contents may be melted. In this way the streaks made by the wires in inoculating the tubes containing gelatine media are got rid of and the microbes are given a chance to grow quickly. After this the tubes are placed in an ice chest until their contents become solid and then they are transferred to a cool incubator regulated to a temperature of from 20° to 22°, where they remain for two days.

The tubes containing peptone water, after they have been inoculated, are placed direct into the warm incubator at 37°, where they are allowed to remain for two days. They are then tested for the presence of indole, using Ehrlich's reagent,

which gives a pink ring where the liquids meet. At the same time the small gelatine tubes are examined to see if any of them contain bubbles of gas and if the colour of the medium has changed, as in the majority of cases it has, for the litmus will have turned red and the neutral-red will have altered its tint and perhaps have a yellow fluorescence.

The Four Groups of Coli-like Organisms.

From a consideration of the above it seems probable that if positive results have been obtained a coli-like organism was present in the original sample of water. Experience has shown in the past that all are not typical, and for practical purposes four groups of coli-like organisms are differentiated by the above tests. Two are regarded as typical and two as non-typical.

In the first case indole is formed and the glucose and the lactose gelatine give positive results, that is, gas formation, but the saccharose tube is unaffected.

In the second instance indole is produced and all the tubes containing gelatine give a positive result.

The third group of coli-like organisms refuses to give a positive result with indole and only the gelatine containing lactose and glucose has bubbles of gas in it.

Lastly, the organism may be one which only decomposes glucose with the formation of gases.

From the point of view as to contamination the first two groups are regarded as giving the most information as to recent pollution. The coli-like organisms from deep wells appear to be mainly non-typical in character. Some coli-like organisms as judged from the



Fig 6—TESTING FOR INDOLE

The tube containing peptone water is tested for the presence of indole by noting if it gives a red coloration with Ehrlich's reagent

presumptive and confirmatory tests, that is, in MacConkey medium and on agar slopes, fail to ferment the sugars in the gelatine tubes or to produce indole in a peptone water tube. Why such should be the case is at present unascertained.

The above is an outline of the method adopted in testing a sample of water bacteriologically and which is supposed to be drawn from a source used for ordinary domestic purposes.

Examining Other Samples of Water.

The procedure to be adopted varies slightly when samples of water are obtained from such sources as contaminated wells, rivers and water suspected to contain a sewage effluent in a bacteriologically unsatisfactory condition.

Well Water.

In the case of a well water from the chalk and not liable to contamination from a river or the sea, one normally would expect to find only very few colonies of microbes growing at blood heat on an agar plate, in many cases less than one per ml. This seems somewhat unusual at first sight until it is remembered that four colonies on a 10 ml. plate mean 0.4 colony on a unit plate.

As a rule

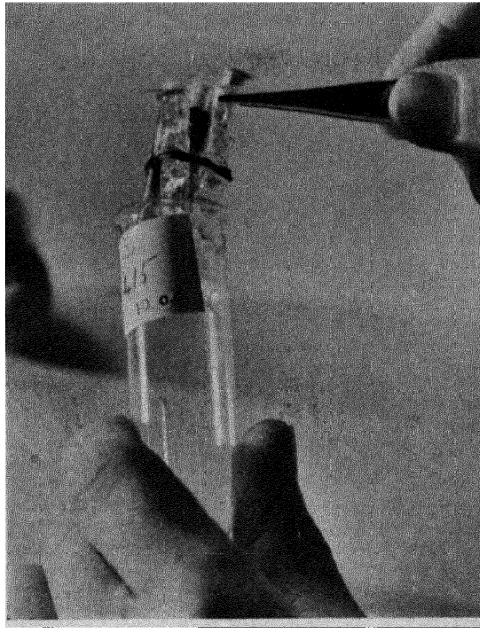


Fig. 7.—A GROUP OF POSITIVE SMALL GELATINE TUBES FOR THE CLOSER EXAMINATION OF THE MICROBES.

there are no coli-like organisms in 100 ml. of well water, or if there happen to be, they are usually found to be non-typical, giving a negative result when tested for indole formation and failing to give bubbles of gas in the gelatine tubes containing glucose, lactose or saccharose. In fact water from the Cretaceous series of rocks is comparatively pure.

Water from a River.

In testing a sample of water from a river, such as the Thames, it can be assumed that specimens of *B. coli*

will always be found in 100 ml. of it, so that 10 ml. is the largest amount which need be taken for examination, but while in a filtered water only 0.1 ml. is the minimum amount of the water sample tested for *B. coli*, in the case of a river water it is advisable to take 0.0001 ml. as sudden floods washing detrital material from the land into the river may add to its bacterial content. It is not usual to find *B. coli* in less than 0.01 ml.

Then also the peptone water tube to which 10 ml. of the water sample was added, when testing water supplied for domestic purposes, is not required as it was only wanted for a rapid test of a cautionary nature.

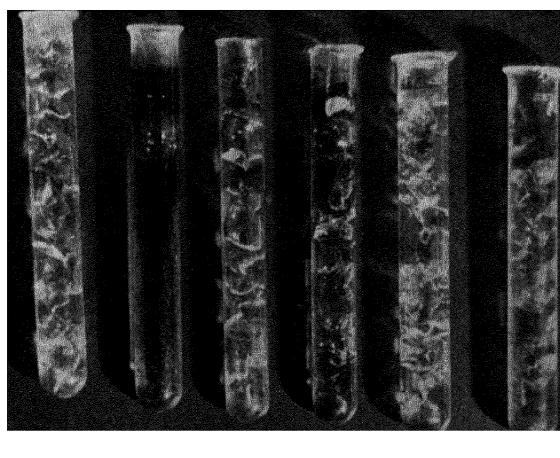


Fig. 8.—A CLOSE-UP OF THE TUBES SHOWN IN FIG. 7.

Examination for Streptococci.

The river

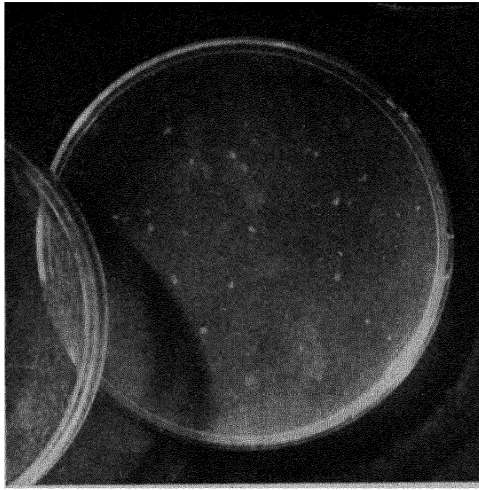


Fig 9—PETRI DISH CONTAINING NUTRIENT AGAR ON THE SURFACE OF WHICH IS GROWING A NUMBER OF COLONIES OF MICRO-ORGANISMS FROM A SAMPLE OF WATER

The agar has been incubated at 37 degrees for 24 hours

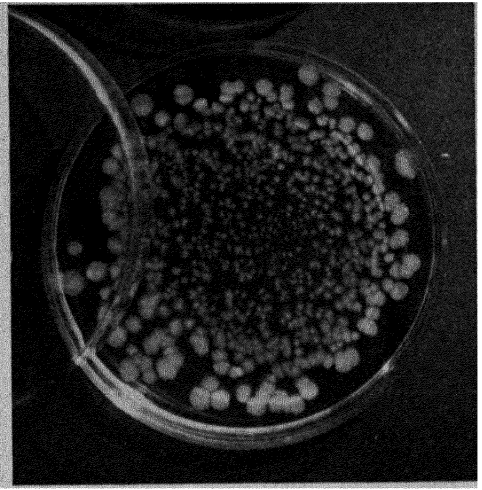


Fig 10—PETRI DISH CONTAINING NUTRIENT GELATINE ON THE SURFACE OF WHICH ARE GROWING COLONIES OF PURE *B. COLI*.

The gelatine has been incubated at 22 degrees for 36 hours

water, in addition to being tested for *B. coli*, should also be examined for the presence of streptococci, as the presence of such micro-organisms affords, in doubtful cases, confirmatory evidence of recent faecal pollution, for, as one authority has written "The presence of streptococci implies animal pollution of extremely recent date and therefore especially dangerous." (A. C. Houston, Twenty-ninth Annual Report of the Local Government Board, 1899-1900, p. 458)

How the Test is Carried Out.

The test for streptococci is carried out as follows. A positive lactose bile-salt tube is selected and from it is taken 1 ml. of the solution, which is added to 9 ml. of sterile water contained in a test tube, and well mixed. Then the tube, now containing 10 ml. of liquid, is placed in a water bath at 60° for about 15 minutes. At the end of this time the tube is taken out, one drop of its contents is let fall on the surface of an agar plate, and then the drop is distributed over the surface by means of a sterile glass rod bent at one end.

The plate is incubated at 37° for 24 hours, at the end of which time there will be seen two easily distinguishable sorts of colonies; the larger ones, usually fewer in number, are most likely *B. coli* and can be neglected. The streptococci form much

smaller but quite characteristic colonies. One or more of these is picked off on a wire and transferred to a tube containing a lactose peptone water medium and incubated for 24 hours at 37°. Faecal streptococci, if present, will give an acid reaction but no gas will be formed in the tube.

At the same time as the lactose peptone water tube is inoculated, the condensation water from a nitrate-agar slope culture is similarly treated and after 24 hours incubation at 37° is examined microscopically, when, if present, short-chained streptococci are easily identified.

To the nitrate agar slope culture a drop or two of metaphenylenediamine solution is added, but no brown coloration should be observed as the streptococci do not reduce nitrates to nitrites.

Pollution of Reservoirs by Sewage from Roads.

The presence of roads near rivers from which a reservoir is filled often results in sewage contamination, more particularly after a spell of dry weather, and the bacteriologist will find in the water of the reservoir things such as anaerobic, spore-forming bacilli, *Bacterium aerogenes capsulatus* and *Bacterium welchii* (or, as some would prefer to call it, *Clostridium welchii*, which may be termed its present official title).

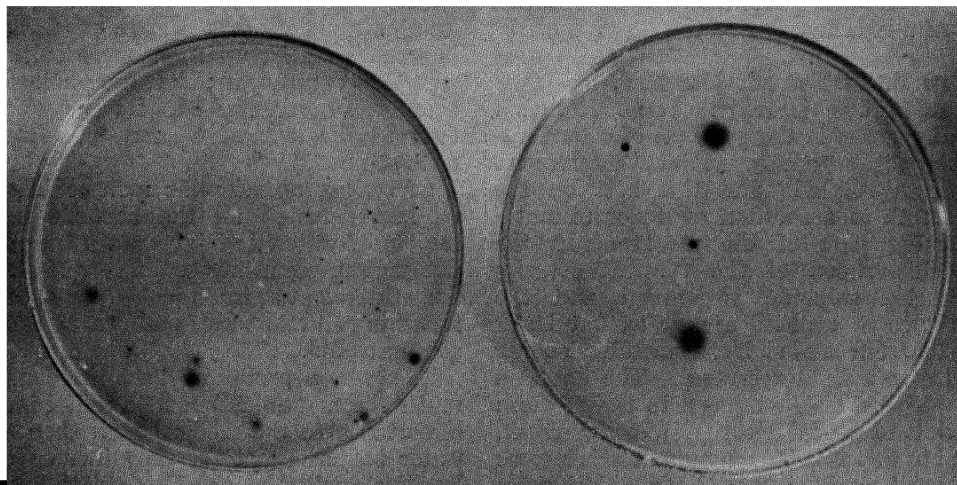


Fig. 11.—PETRI DISH CONTAINING SPECIAL MEDIUM FOR THE DETECTION OF *CLOSTRIDIUM WELCHII*. This bacterium reduces the sodium sulphite present to sulphide. This in its turn acts on the bismuth salts present with the formation of bismuth sulphide of a characteristic brown colour. The colonies are 5 mm. or more in diameter.

This micro-organism is likely to be accompanied by another one, the *Bacterium enteritidis sporogenes*.

Detecting the Presence of *Clostridium Welchii*.

The method adopted for detecting the presence of *Clostridium welchii* is as follows: 10 ml. and 1 ml. of the water to be tested are added to freshly boiled litmus-milk contained in test tubes. The mixture of milk and water is heated to a temperature of 80° for ten minutes. This procedure will kill all but spore-bearing organisms. The tubes are then incubated anaerobically, that is, free from air, at 37° for three days, when, if *Clostridium welchii* is present, there will be the appearance of "stormy fermentation" in the tubes.

Another Test.

Another mode of detecting the *Clostridium welchii* is to add samples of the water to agar-glucose plates to which is added when the agar is liquid a mixture of sodium sulphite and ferrous sulphate. 40 ml. of the medium is poured into a large Petri dish and a similar amount of the water sample added. The whole mixture is allowed to solidify, after which 20 ml. of agar is poured on the top and is soon solid. This will ensure anaerobic conditions of growth of the micro-organism.

The plates are incubated at a temperature of 45° for from 24 to 36 hours, at the end of which time the colonies of *Clostridium welchii* appear as large black spots 5 mm. or more in diameter in the depth of the medium.

In testing the sample of river water by noting the number of colonies which grow on agar, it is now customary to incubate the plates of agar at both 22° and 37°. Many more colonies will be found on the plate at the lower temperature.

A sample of sewage can be regarded as a highly polluted river water. Consequently it must be tested for *B. coli* in high dilutions and special attention paid to the examination for *Clostridium welchii* and streptococci.

Examination for Typhoid Bacillus.

In addition, it will frequently be necessary to examine the sample for the presence of the typhoid bacillus and other pathogenic organisms. This is a procedure only adopted in cases of necessity, for frequently when the water bacteriologist is informed of the likelihood of the presence of the pathogenic organism the danger of infection has been much reduced, as also the chance of finding a pathogenic organism, for bacilli of the typhoid group are comparatively delicate compared with *B. coli*. The typhoid organism is found only rarely in water.

The following procedure can be followed for its isolation.

How *B. Typhosus* is Identified.

Advantage is taken of the fact that *B. typhosus* in the presence of a fermentable sugar reduces sodium sulphite to sodium sulphide and this acts on the bismuth in a solution of liquor bismuthi forming part of the medium. In the neighbourhood of the typhoid colonies bismuth sulphide is formed and the colonies of typhoid appear as flat black specks surrounded by a metallic-looking halo on a lighter ground. The addition of the dye brilliant green to the medium will tend to inhibit the *B. coli* present, and in this case the medium used is lactose bile-salt agar, on which typhoid colonies grow most easily.

The presence of the typhoid bacillus if isolated must not rest on one experiment but needs confirmation, so more cultural tests are employed; its morphological characters are studied, its behaviour towards agglutination and absorption tests are noted.

Of course, no scientific man could say he had detected all the bacteria in a sample of water, but the ones mentioned above are those most usually sought after. Sometimes leptospira is looked for as it is found in soil and water and can be easily demonstrated.

The whole group of bacteria classed under the name of *Salmonella* are of more importance to the medical man than the water bacteriologist for they include the *Bacillus typhosum*, the *B. paratyphosum* B., the *B. enteritidis* and the *B. aertryke*.

MUMMERY AND BISHOP'S TEST FOR LACTIC CASEIN

LACTIC casein is best treated by Mummery and Bishop's test, which deserves to be more widely known, as it yields more reliable results than with the Dahlberg or Zoller method.

Materials Required.

Borax Solution.—20.833 gm. of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ dissolved and made up to one litre.

Indicator.—One decigram of brom-thymul blue macerated with 3.2 ml. N/20 NaOH and made up to 250 ml.

Standard Buffer Solution.—Made up according to Clark and Lub's formula with KH_2PO_4 and NaOH (J. Biol. Chem., 1916, 25, 497).

Water.—Distilled water with pH—6.0

obtained by allowing the water to absorb CO_2 till the pH drops to the figure named.

Method.

Two gm. of 30 mesh lactic casein is placed in a $\frac{3}{4}$ -in. test tube with 12 ml. borax solution, then placed in a water bath at 70°C . and stirred at intervals for 45 minutes. If solution is not homogeneous after this, incomplete solubility is indicated. Make the solution up to 100 ml. with water and pipette 1 ml. into another tube with 10 ml. water. To this dilute solution add 5 drops universal indicator. The pH of this solution indicates the ease of solubility of the casein.

THE CANNING INDUSTRY

RAW MATERIALS, CONTROL TESTS AND ANALYTICAL METHODS

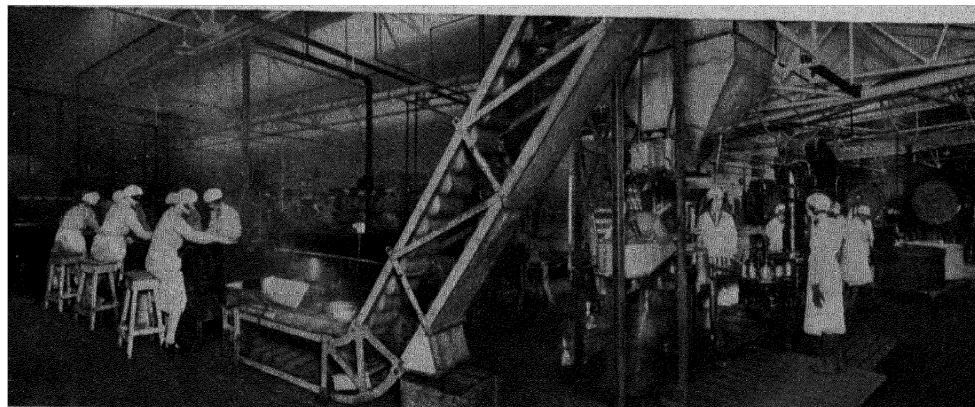


Fig. 1.—A CORNER OF MESSRS. CHIVERS'S VEGETABLE CANNING INDUSTRY.

THE ideal before the canner is to produce an article in which the natural colour, flavour, texture, and appearance of the fruit and vegetables are retained indefinitely. The natural vitamin potency must equally be preserved. A happy combination of scientific research and commercial practice has enabled the canning process to advance considerably towards this ideal. Details of this process are perhaps best described under three heads—the container, the raw materials, and the process of preparation itself. Control tests and analytical methods will be given later in the article.

The Container.

This is a very important item. Two alternatives are available—the glass jar and the tin can. The former has several advantages, but the economy of the latter more than offsets these and makes the tin can the popular container.

The so-called "hygienic" can has been materially improved in the last decade. It consists of a cylindrical vessel of tin plate (with or without an internal coating of lacquer) with double-seamed-wheeled-on ends, the joints of which are made without

solder. Mechanical accuracy and efficiency, together with rubber gaskets, ensure air-tight joints.

It has long been known that the complete and uniform coating of the base plate with the film of tin was essential for success, but recent research points to the importance of the composition of the iron base plate.

The Use of Lacquer.

Even the best tin plate shows under test pinholes of bare base metal, and the effect of this on fruit and vegetables gave rise to the use of lacquer. Suitable gums and gum resins are dissolved in mixed solvents and, prior to making up, the plate is evenly coated with the mixture, which is then dried and hardened by "baking" at from 375° to 400° C. for 20 to 40 minutes. In subsequent handling in making up the can every care is taken to avoid damage to this protective film.

The prime function of the lacquer is to prevent the formation of hydrogen by the complex interaction of container and contents, but it is now known that such prevention is more apparent than real. On the other hand, contact with tin

results in an unfortunate change in shade of the red (anthro-cyanin) colouring bodies in fruit from their attractive natural colour to a somewhat objectionable purple. The lacquer film prevents this trouble and for this reason is still necessary with fruits of red shades of colour, but it is no longer used for green or yellow fruits.

The lacquer varies in composition according to its use—whether for fruit or vegetables. It must have no effect on either the colour or flavour of the can contents, must be quite insoluble, and must not peel off on prolonged storage. While quite hard, it should not be at all brittle, but sufficiently plastic to avoid cracking and other damage during the manufacture of the cans.

The Raw Materials.

The fruit and vegetables to be canned and, in addition, sugar, salt and water (and in some cases a little fruit acid and, where needed, a trace of suitable artificial colour) cover the range of raw materials.

White, refined sucrose is employed. Preference is given by some authorities to sugar of cane rather than beet origin. A sugar "blued" with ultramarine should be avoided, as otherwise discolorations due to the formation of sulphur compounds from the sulphur thus introduced will result.

Salt of high chemical and bacteriological purity only is used in vegetable canning.

Any good drinking water supply is suitable for canning, provided it is not unduly hard.

The Supply of Fruit and Vegetables.

With fruit and vegetables—raw materials for canning—it is important to consider the source of supply, the matter of freshness, the variety and quality, considerations of cleanliness, etc.

It is fatal to imagine the cannery can thrive on cull fruit or market excess in times of glut. Successful canning calls for fruit or vegetables of selected variety from suitable soil and harvested as to time and manner more from the canner's and less from the farmer's point of view than is normally the case.

The Importance of Freshness.

The cannery should be situated in proximity to the district in which the raw material is grown. Freshness is a prime

necessity. A popular canning aphorism in America is: "There are just two days when peas are fit for canning—the day they are ready, and the day before." Admittedly, freshness is a comparative term, but the less time allowed for post-picking changes in the fruit, etc., before all life action is killed in the canning process, the better the final result. Mould spores are always present with ripening fruit and develop very rapidly after picking. While most moulds are killed in the canning process, it is certainly undesirable to regard the fruit can as a mausoleum for moulds. A consignment of ripe strawberries for canning can easily suffer considerable damage from mould development in 20 hours in a ventilated box railway truck during transit. These, then, are further arguments for canning really fresh fruits.

Again, with peas—bacterial development and enzymic action during transit to the cannery, and any delay in handling on arrival, may easily give rise to deterioration in flavour and problems of the "flat-sour" variety. In fact, freshness determines very largely the degree of fine bouquet and flavour, as well as (with fruit especially) the firmness of texture which is the pride of the canner's art—always, of course, assuming that picking has occurred at the correct stage of maturity.

For canning, fruit should be picked just before it reaches the "dessert" stage of ripeness. If picked too soon the cells and tissues are not sufficiently developed and the fruit shrivels in the sugar syrup, and of course the greener the fruit the less the flavour. On the other hand, if the point of maximum flavour development be taken as standard for picking, the texture will be too soft and the fruit will disintegrate in handling and processing. The optimum conditions for canning in relation to maturity must be learned by experience—they vary with different fruits.

Condition of the Fruit.

One final point to be remembered is the "condition" of the fruit for canning. Freshness and correct degree of maturity has already been stressed. The fruit may pass on these counts but may still be unfit for canning because of bruises, blemishes, faulty shape, contamination with earth, dirt, leaves, stalks, and other extraneous matters.

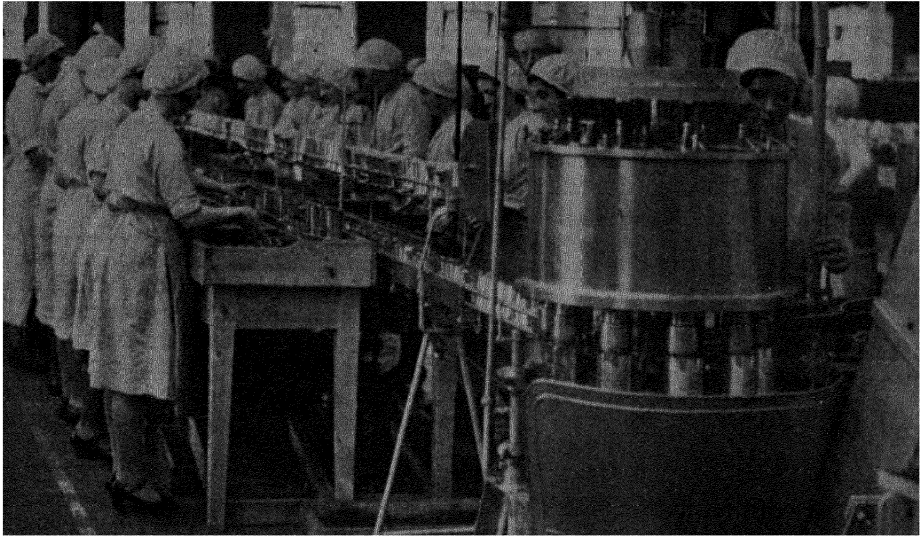


Fig. 2.—FILLING THE CANS WITH FRUIT.

The cans are filled with fruit and placed on to the conveyor which carries them along to the syrup machine.

Preparation of Fruit.

For these reasons fruit and vegetables pass through a number of important preparation processes prior to the process of canning proper. These include "nubbing," "strigging," "shelling," "snipping," "pitting," as well as hand sorting, washing and grading.

Gooseberries.

Gooseberries, for example, need to be "topped and tailed," i.e., to have the remnants of the calyx removed from one extremity and the stalk from the other. This is termed in canning circles "nubbing." It is done by placing the fruit in an open-topped stationary iron cylinder fitted with a revolving bottom of such design that a wave-like rotary motion is imparted to the mass of fruit. The whole interior of the machine is lined with fairly rough-grained carborundum and during use is drenched with a spray of cold water. The abrasive action is such that first the "nubs" are removed from the gooseberries with quite negligible damage to the skin, but if the action is continued the skin is almost entirely removed. The fruit is, of course, removed from the machine at the point of maximum loss of tops and tails and

minimum skin damage. It is a very satisfactory operation with green firm fruit.

Black Currants.

Black currants need 'stalking'—this is done on a "strigger," which consists of a slightly inclined tray, the bottom of which is formed by a series of parallel bars through which rotate hooked metal fingers. The tray oscillates, and currants placed at the top end are impelled forward—so passing over the metal fingers which engage the stalks and drag them through the bars, which are so spaced that the fruit is retained above.

Peas.

Peas are harvested together with the vine on which they have grown and carted intact to the cannery. The pea viner receives the mass direct from the farmer's cart and delivers shelled peas at one outlet and the vines and empty pea-pods at another. The removal of hand-picked peas from the pods is effected in a "sheller," which is a rotating device in which the pods receive a "brushing squeeze" so adjusted that whilst the pod is split and rubbed open, the peas are not crushed, bruised, or damaged.

Beans.

No domestic kitchen welcomes the tiresome job of preparing beans for cooking. There are no strings to remove from canning beans (a stringless variety is specially grown), and the tops and tails are removed in "snippers." These consist of revolving, horizontal cylinders fitted internally with helical baffles and with the walls perforated with many suitably shaped holes. As the beans traverse this cylinder the ends project through these holes and are sliced off with an external oscillating knife suitably attached. The beans are then fed into finger-like hoppers of the slicing machines, the revolving knives of which quickly reduce them to uniform slices.

"Pitting."

Stones are removed from cherries, etc., on the manufacturing scale by "pitting." The fruit falls into holes placed in regular rows in a belt, which places it in position beneath a series of fine metal prongs so spaced that while the fruit is held firm and suffers the minimum of damage the stone is pushed out through the flesh and skin.

All this mechanical treatment needs supplementing with hand sorting. Indeed, there is no substitute for this for the removal of blemished, damaged, under or over-ripe fruit, adhering stalks, leaves, etc. With vegetables, too, a satisfactory pack calls for a good deal of hand work in trimming and completing omissions of the mechanical washing, etc., due to irregular shape. Potatoes, celery and spinach are examples which may be cited.

Washing.

Wherever possible, fruit for canning should be washed. Strawberries, for example—even from beds that have been well strawed—often carry an appreciable amount of grit and earthy matter from the soil. The amazing amount of sandy sludge taken from a large-scale mechanical strawberry washer at the end of a day's run is very convincing proof of the need for the careful washing of fruit for canning. Pea-washing plant ingeniously removes heavy and sandy matters—and at the same time light, floating extraneous bodies are washed away, and the peas cleansed of gummy and similar substances. Washing machines vary in their design according to

the fruit they are intended to handle. Some are built on the principle of a belt on which the fruit is carried beneath a series of jets of water, in some the fruit revolves on a rubber or fibre mat under water, and some again employ a revolving brush idea to assist a water spray.

Grading.

It is obviously desirable to have fruit of uniform size in a given container, and as British fruits vary considerably in dimensions, "grading" or sorting according to size is a necessary operation. With strawberries and raspberries this must be done by hand, but in the case of gooseberries, cherries, plums, apples, carrots, peas, etc., mechanical graders are used. These again vary very widely in design.

One design of apple grader consists of a series of counterbalanced trapdoors weighted with standard-sized fruit. The apples to be graded pass over or fall through a given trap according to weight and so are separated into grades.

Plums are graded on machines fitted with wooden slats, the openings between which vary in width as the slats progress along the machine. The falling fruit is received into chutes beneath the slats. A device is fitted to give a spinning motion to individual plums to compensate for their irregular shape and so ensure uniform grading. Apart from this device, it will readily be seen that a plum lying on a slat with its longitudinal axis at right angles to the slat opening would pass to a larger grade than the same-sized fruit which happened to be with its transverse axis across the opening.

Peas are comparatively easy to grade owing to their spherical form. A revolving cylinder perforated with holes the size of which increases in regular stages from the inlet to the discharge end, and through which the peas pass, is a simple but effective form of pea grader.

National Mark Standards.

In the case of cans carrying the National Mark the following regulations as to grading and size of fruit must be observed:—

NATIONAL MARK GRADING STANDARDS.
(Measurements are of maximum transverse diameter.)
Grade.

Fruit.	Gallon size can.	Small.	Medium.	Large.
Gooseberries ..	10/16"	12/16"	14/16"	Over 14/16"
Cherries ..	—	13/16"	15/16"	15/16"
Plums ..	—	21/16"	23/16"	23/16"

Filling the Fruit into Cans or Bottles.

After these many preliminary operations the fruit is now ready for filling into cans or bottles. In the main, this is done by hand. Mechanical filling must reckon with the necessity of filling the container to its utmost capacity with the fruit or vegetable—consistent with the avoidance of crushing. With peas this is possible, and generally they are filled mechanically, but the irregular shape of most fruits and vegetables calls for hand work to get a full container. This is especially so with bottles, where the natural shrinkage which occurs in the cooking process, and which is so easily apparent in a glass container, gives an impression of under-filling. To offset this, fruit for bottling and for so-called "solid pack" cans is "blanched" before filling. Many vegetables, too, are "blanched" before filling into cans.

"Blanching."

"Blanching" is simply a partial pre-cooking. The fruit is plunged for a given time—from half to, say, five minutes, according to variety—into water at from 180° to 200° F., and then immediately cooled by immersion in cold water. The object is merely to soften the texture and so enable a greater weight to be pressed into the container without damage to the individual fruit.

With vegetables, "blanching" has a variety of functions. Shrinking, removal of air, and in some cases, as with peas, the removal of undesirable flavouring substances.

Addition of Liquor or Syrup.

The liquor, or syrup, is next added—usually mechanically. It is always added as hot as possible. It is also important that any liquid added should be clear and bright—it is usually filtered before use. Any colouring matter needed for a given pack is dissolved in and added with this liquid. The amount of liquid added is regulated so that in the finished can there is from $\frac{1}{16}$ in. to $\frac{1}{8}$ in. "headspace," i.e., space void of liquid or fruit.

Fruits (especially in large cans) designed for use in tarts and cooking generally are usually packed in water. The popular pack is, of course, in sugar syrup so that on opening the can the contents are ready for immediate consumption without any addition or further cooking. Great care

is taken to keep the sugar concentration of the syrup constant and at a fixed or standard strength. This is arrived at mainly by considerations of flavour, which are influenced by the acid and general character of the fruit used.

Recommended Syrup Strengths.

The following syrup strengths are recommended to packers using the National Mark:—

Fruit.	Syrup Strength (Degrees Brix).
Cherries (white)	.. 35
Apples	.. 40
Plums	} 45
Gooseberries ..	
Morella cherries	
Blackberries ..	
Strawberries ..	} 50
Raspberries ..	
Black currants ..	
Red currants ..	
Loganberries ..	

It is to be remembered that in the finished can a state of equilibrium will slowly occur within and without the fruit by osmosis. The sugar syrup is diluted with the juice passing out of the fruit cells, and the concentration of the soluble cell contents rises as sugar enters. The stronger the syrup that is used, the greater the tendency for the fruit to shrivel (which should be avoided) and the greater the final shrinkage. At the same time, sugar has the effect of making the fruit texture firmer and of imparting a desirable brightness and sparkle to the appearance of the fruit. It is to its homogeneity and to the controlled effect of sugar on texture that canned fruit owes its superior flavour and palate effect—a result which direct cooking can never approach.

The composition of the liquor for vegetables is usually a combination of sugar and salt, generally in the proportion of 2 per cent. sugar and 2 per cent. salt.

The Fruit is Filled into the Can Cold.

The actual fruit or vegetable is filled into the can cold, but it is highly desirable that the can and contents should attain as nearly as is practicable the cooking temperature prior to sealing on the lid. Cooking, of course, takes place after the can is sealed.

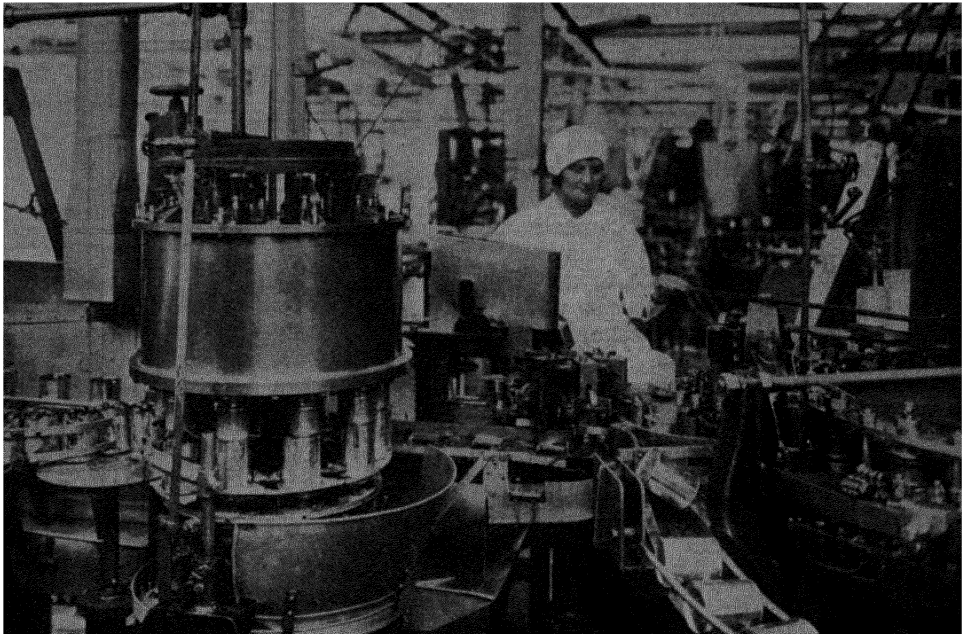


Fig 3 —AFTER THE CANS HAVE BEEN FILLED WITH FRUIT AND THE SYRUP ADDED THEY ARE SEALED BY MACHINERY WITHOUT THE USE OF SOLDER.

The Exhauster.

While some heat units have been introduced by the hot liquor, more are needed. "Exhausting" is therefore the next process. The lid is placed loosely in position and the can enters the "exhauster," which is a closed tank fitted with revolving wheels, or conveyor chains, or other means to cause the cans to progress forward through water kept at a minimum of 200° F. The cans are immersed in the water to at least 75 per cent. of their height. The speed of the conveyor or wheels is regulated to allow a definite time for exhausting. This varies from 1 to 10 minutes, according to the size of the can and the variety of fruit.

Like "blanching," "exhausting" serves at least a triple purpose:—

- (1) It helps to remove dissolved oxygen.
- (2) It ensures a higher final vacuum in the can.
- (3) It assists the cooking and sterilising process.

Why the Presence of Oxygen is Undesirable.

The presence of oxygen in a can of fruit

is highly undesirable—as has been shown by the American School of Canning Technologists. A very complex interaction between container and contents, resulting in the generation of hydrogen and producing internal pressure indicated by bulging ends, is one of the major troubles of fruit canning. Many explanations have been put forward, but more research is needed before the phenomenon can be satisfactorily explained. It does appear that oxygen plays some part, and therefore it is desirable to remove it as far as possible prior to sealing on the lid.

Vacuum.

A good "exhaust" raises the internal temperature, and air and other gases in the head-space are largely displaced by expansion and replaced by steam. Sealed in this condition a can will show a good vacuum on cooling. Under proper canning conditions a vacuum of 10 to 14 in. of mercury should result. Attempts have been made to do better than this by sealing the can under a mechanically obtained vacuum, but in practice the vacuum obtained by the "exhausting"

method is usually much better. The production (within limits) of hydrogen in a can is no detriment to the contents, but nevertheless ranks as spoilage owing to bulged can ends. A good vacuum means, therefore, among other things, that a fair production of hydrogen may occur without bulged ends, i.e., without the commercially so-called "half-blown" effect.

The raising of the temperature of the can contents during "exhausting" helps the attainment of the thermal death point of yeasts, bacteria, etc., under canning conditions, earlier in the cooking process and so helps to ensure the sterility of the pack.

Sealing the Lid.

The "exhausted" can now passes to the "double seamer"—which machine seals the lid securely to the body of the can. It is most important this operation should be mechanically accurate and perfect. The flange of the can body and the outer rim of the lid—between which is sandwiched a gasket of rubber latex—are given a double fold and then squeezed tightly together. This is done by causing the flange edges to impinge on wheels of suitable contour revolving at high speed, simultaneously revolving around the can.

Faulty adjustment of the wheels or rolls of this machine results, on the one hand, in fracture or cutting of the metal, and on the other, in a joint insufficiently tight. Both faults mean spoilage. Expert knowledge is required to detect the minute faults in double seaming which, in their mildest form, are known as "breathers"—that is, joints which, though apparently quite air-tight on test, yet under the strain of cooking and cooling admit a trace of air or water and with it micro-organisms, with consequent spoilage.

Cooking or "Processing."

Cooking, or "processing" in canning parlance, are terms for the next stage of cannery practice, the meaning of which is self-evident.

From the consumer's standpoint the fruit is cooked. From the canner's it is "processed," i.e., cooked and sterilised. These are the two main functions of this department of the cannery.

The fruit or vegetable must be whole and cooked to the optimum point of tender firmness. Such a result needs rigidly controlled conditions of time and temper-

ature—especially when the factor of sterility is added. Fortunately, with the pH values incidental to fruits in sugar, most yeasts, moulds and bacteria are killed within conditions compatible with good cooking. With vegetables, which have a higher pH than fruit, pressure cooking, with a consequent higher temperature, is essential to ensure commercial sterility. For this reason the home canning of vegetables is dangerous and to be deprecated. American experience has shown the serious danger of botulism in home-canned vegetables. The cellular structure of vegetables being firmer than that of fruit, this additional cooking is no detriment.

Bacteriological Checks are Advisable.

It must not be assumed from the above that bacterial troubles in canning are unknown. No can of fruit should leave the factory until sufficient time has elapsed to ensure freedom from fermentation due to yeast cells which may have survived. A laboratory bacteriological check on test cans of vegetables is also a wise item of factory routine. Resistant moulds, such as *Byssochlamys fulva*, too, are known, and "flat sours" in canned peas are produced by bacteria which have escaped death in the cooking process.

Types of Cookers.

Obviously, cookers for fruit must be quite different in design to those for vegetables. There are two main types of the former—in one the cans are propelled through a heated chamber, without themselves revolving, and in the other the cans themselves revolve during the entire cooking process. The advantage of the latter is at once apparent when it is remembered that the more uniformly the contents of the can are heated, the better the result. The quantity of fruit (as, for example, close-pack apples) in the can hinders and sometimes prevents convection currents, and the penetration of heat by conduction only is a slow process. When, however, the can contents are gently agitated, quicker and more uniform heating results. At the same time care must be exercised not to carry the agitation too far, particularly during the later stages of cooking, when the fruit is more tender and therefore liable to disintegrate. To ensure sterility, the *centre* of the can must reach

a given temperature, but at the same time the temperature of the fruit adjacent to the sides of the can must not rise unduly high or over-cooking may result.

In practice it is not possible to obtain ideal conditions from each point of view, but a satisfactory compromise is readily obtained.

The Rotary Cooker.

A rotary cooker for fruit consists of an outer cylindrical jacket surrounding a revolving metal cage into which the cans are fed at the loading end. The design of the cage is such that the cans follow a helical course towards the outlet end of the cooker, themselves rotating in the process. Upon entering, the cans are immediately immersed in water maintained thermostatically at the required temperature, and removing facilities are placed at intervals along the cooker, so that the time a given can is immersed in the hot water may be determined at will without altering the speed at which the cooker rotates. Further modifications of time of cooking are controlled by varying the speed of rotation.

Cooking Times and Temperatures.

Cooking times and temperatures are fixed by a variety of factors, among which may be mentioned the size of the can, the kind of fruit, and the degree of ripeness.

For practical working, the exact conditions must be fixed by an actual test, and correct cooking maintained by opening test cans at intervals during the day's run. The temperature attained in the centre of the can must also be regularly checked. One method of doing this is to fix a small thermometer, just covering the required range, and fitted with a maximum temperature indicator in the centre of a test can, suitably marked for identification purposes. An approximate guide to cooking times at a temperature of 210° F. for some of the principal fruits grown in this country is given in the table below:—

APPROXIMATE COOKING TIMES IN MINUTES AT 210° F.

Fruit.	In stationary cooker	In rotary cooker.
Gooseberries ..	25	13
Strawberries ..	20	10
Raspberries ..	15	7
Black currants ..	30	15
Pershire plums ..	18	9
Victoria plums ..	20	10
Damsons ..	25	13

All vegetables are cooked in retorts under pressure. The closed cans are filled into perforated metal crates which are placed by mechanical means into iron retorts where they are heated by steam to at least 240° F. for 40 minutes. Here again the time of cooking varies with the size of the can and particular vegetable being handled.

Many attempts have been made to design a continuous pressure cooker, but so far such cookers have not been generally adopted in commercial practice.

The Cooling Process.

Cooling is the next process. It is important that when the contents of the can are cooked and sterile, the temperature should be lowered as quickly as possible to at least 100° F. Unless sufficient cooling is promptly carried out, not only does the cooking process continue to some extent, but so-called "stack burn" may occur, for imperfectly cooled cans stored in large stacks retain their residual heat for many hours, and even days. Again, faulty cooling accentuates half-blown or hydrogen swell troubles.

Coolers are of varying design, but are often similar in construction to cookers; indeed, vegetable cooking retorts are often fitted with a cold water supply and used as coolers. Care must be taken to avoid straining the cans by too sudden changes from pressure to vacuum. Such strains in a mild form sometimes cause minute temporary openings through which a little cooling water gains access to the can, and this introduces infection with micro-organisms. The bacterial purity of cooling water is therefore important.

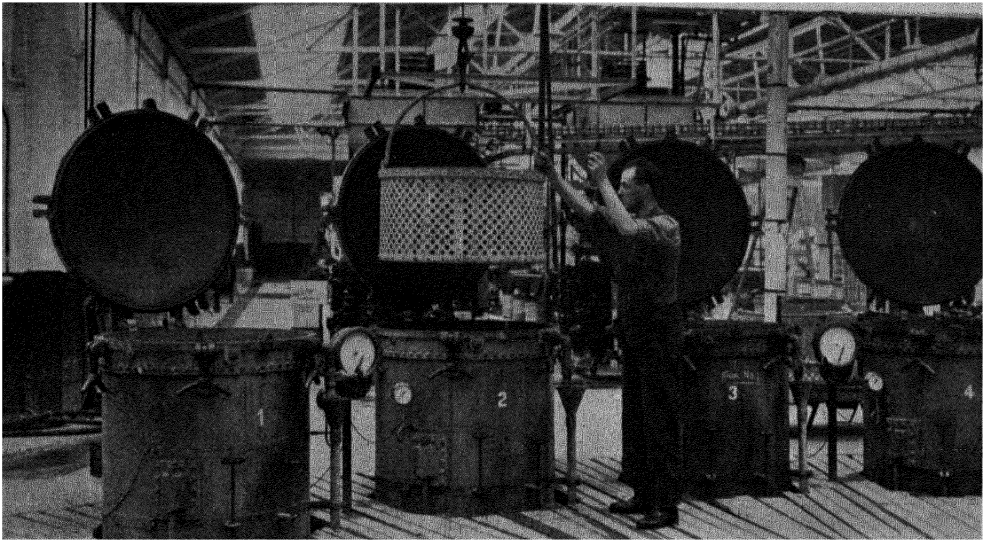
Air cooling in conjunction with a cold water spray is effective in removing heat from cans by means of the latent heat of evaporation. This principle is employed in commercial work in the "tunnel" system of cooling cans.

Over-cooling involves the danger of wet cans being placed in store and paves the way for rusting troubles.

The cooled cans are now ready for the store. This should be a cool building, so ventilated that the humidity of the air in contact with the cans should be low enough to prevent the formation of rust, irrespective of outside atmospheric conditions.

PHYSICAL AND CHEMICAL CONTROL TESTS.

The canning and bottling industry



"The Industrial Chemist."

Fig. 4.—BATTERY OF COOKING RETORTS IN MESSRS. CHIVERS VEGETABLE CANNING FACTORY.

involves highly technical operations. It therefore calls for numerous control tests both physical and chemical. The reader is referred to technical books on canning for a complete range of suitable tests, and, indeed, beyond these it is desirable in each cannery to devise special checks on plant operations which must of necessity be suited to the needs of the particular occasion.

Since the cans prepared ready for filling are supplied to the cannery, the chemist here can only carry on the control tests, which should start with the tin plate from which the container is made. Manufacturers produce this in graded "weight" (this is a trade expression denoting the thickness or gauge of the sheets of base metal), and it is important that any given grade should be free from the effects of irregular rolling. Uniform thickness of plate ensures the cans being of uniform strength and character.

Testing Quantity of Metallic Tin per Square Inch of Plate.

Tests for the quantity of metallic tin per square inch of plate are often carried out. This may be done by dissolving the tin in a mixture of hydrochloric acid and antimony tri-oxide, but it is far more important to have a film of tin comparatively free from pinholes than to have a

more or less porous film of a given thickness. Tests for porosity are therefore of greater importance than the determination of the actual tin per square inch.

There are various means of determining this lack of continuity of the tin coating, but the following method finds general acceptance for ease, speed and reliability.

Samples of the plate are cut into squares with about 4 in. sides. These are carefully cleaned with carbon tetrachloride, and finally with anhydrous acetone. A solution is prepared by dissolving $7\frac{1}{2}$ gm. of gelatine in water, adding to it 1 ml. of freshly prepared 5 per cent. aqueous potassium ferri-cyanide and finally making the whole up to 100 ml. When cold, this solution is, of course, a jelly. The hot liquid ferri-cyanide solution is poured on to the tin plate squares and the film allowed to set. After one hour the number of blue spots of ferrous ferri-cyanide (indicating direct contact between the reagent and surface of the base metal) visible to the naked eye are counted.

How the Results of this Test are Expressed.

The results of this test for porosity may be expressed as follows:—

Up to 12 spots per sq. cm.	Normal plate.
From 12-20 " " "	Fairly porous plate.

From 20-28	„	„	Porous plate.
Over 28	„	„	Very porous plate.

An Alternative Method.

An alternative method is to produce spots of rust on the squares of tin plate by allowing them to stand immersed in hot distilled water for a given time. This test, however, takes longer to perform than the ferri-cyanide test outlined above.

Concentration of Sugar Syrup.

As pointed out earlier in this article, the concentration of the sugar syrup in which the fruit is canned and the amount of acid present have an important bearing on the flavour and quality of the final pack. These two factors lend themselves readily to analytical control, and routine tests are regularly carried out in all well-appointed factories.

Simple Hydrometer Test.

It is customary for the foreman approximately to adjust the strength of his sugar syrup with a hydrometer. As this is done on the boiling syrup, the final adjustment must be made by the laboratory.

The Refractometer Test.

To do this, a sample of the syrup is cooled to a standard temperature, and the total soluble solids ascertained by measurement of its refractive index. The cooling is conveniently effected by pouring the syrup into a funnel commanding a vertical spiral condenser. The bore of the condenser tube should be sufficiently restricted to ensure the rate of flow being consistent with the necessary degree of cooling. By employing an "Abbe" type of refractometer with a scale graduated for percentages of sugar, these tests can be performed very quickly by a junior assistant. There is, therefore, no excuse for syrup of incorrect strength being used in any modern canning process.

The determination of acidity is described later under tests for the finished product.

Weight and Volume.

It is readily obvious that the weight and therefore volume of fruit in a given can is complementary to the amount of syrup that can subsequently be added, and that a decrease or increase of the former reacts very considerably upon the proportion of sugar present in the final pack, and conse-

quently upon the flavour. It is not possible in commercial practice to weigh the contents of every individual can, but apart from mechanical aids supplied to operatives who actually place the fruit in the cans, a laboratory check on the fruit in sample cans withdrawn from the canning line immediately prior to syrupeing has a wholesome influence in maintaining a standard pack. In the same way, similar control should be exercised in the times and temperatures of exhausting, cooking, cooling, etc.

"Cut Out" Tests.

A further series of tests is carried out on samples of the finished pack. These are known as "cut out" tests. It is not easy to obtain representative samples of the day's run, as fluctuations in the operating of the canning line may easily occur between the taking of samples, and so pass unnoticed. The frequency with which such samples should be taken must, therefore, be governed to some extent by local circumstances, but for usual control purposes it should be sufficient if duplicate sample cans are withdrawn from the discharge end of each canning line for, say, every 5,000 cans produced. One can is tested immediately, and the second is retained under normal storage conditions for a given period (usually about three months), and the same series of tests then applied.

Degree of Vacuum.

The degree of vacuum within the can is a prime indication of correct canning practice. It is, therefore, checked on each test can. A special vacuum gauge is used for this purpose. It consists of a delicate gauge of the orthodox circular type, the connecting tube of which terminates in a tubular needle point surrounded by a pad of pliable rubber. The whole is so dimensioned that, when the point is pressed into the lid of a can, the rubber forms an effective seal around the resulting opening, ensuring an accurate registration on the gauge of the vacuum within the can.

The ends and sides of the larger size cans are necessarily more flexible than the smaller ones. This flexibility affects the vacuum within the can, and allowance must be made for this in interpreting the results of a vacuum test. The smaller-sized cans when first packed should show

a vacuum of at least 15 in., but with the larger cans it seldom rises above 8-10 in. Vacuum tests on cans three months old will show slightly less than the above figures, but any indication after this period of a definite and obvious fall in the degree of vacuum should be regarded as a warning of either internal gas generation or a leaky container—both faults occasioning spoilage and rendering the pack unsaleable.

Head Space—

In dealing with practical canning instructions in the paragraph describing the addition of sugar syrup to the can, mention was made of the "head space." With vegetables, sufficient "head space" is essential, as otherwise very serious deterioration and even buckling of the side seam of the can will take place during cooking and cooling operations. Again, with fruit the presence of sufficient "head space" is important for the maintenance of the original vacuum during the normal period between packing and final consumption. Hydrogen is generated very slowly as soon as the can is packed, and insufficient "head space" with a given volume of hydrogen production obviously lowers the vacuum more quickly than a "head space" of normal proportions, and so tends to give rise to "half-blown" effects sooner than is desirable.

—And How it is Measured.

A measurement of the actual "head space" is therefore carried out on each test can. This is done by placing a straight edge across the flanges of the opened can and measuring the distance between this and the surface of the liquid. An appropriate subtraction from this figure must be made to allow for the depth of the flange, and the result is usually expressed in sixteenths of an inch.

The total weight of the contents of the can is taken, and the syrup is then allowed to drain for 30 seconds from the fruit, and the weight of this and the fruit observed.

Classification of the Appearance of a Pack.

The fruit and the syrup are again united, and the appearance of the pack critically noted. It may be described as follows:—

Very Good.—If the fruit is unbroken, well cooked, and the syrup clear and bright.

Good.—If the fruit is not badly broken, is well cooked, and the syrup clear and bright.

Fair.—If the fruit is somewhat broken, and the syrup fairly clear.

Poor.—If the fruit is broken or ragged, over-cooked or under-cooked, or if the syrup is cloudy.

Except in the case of the smaller fruits such as black currants, the number present in the can is noted, and remarks are made concerning uniformity of grading, freedom from extraneous matter and misshapen or blemished fruits. There is no chemical or physical substitute for the human palate, and judgment must be made by tasting whether the can is up to standard for fruit flavour. The flavour of the pack as a whole, having regard to the due relationship of sweetness and acidity, is also recorded.

Testing Acidity of the Syrup.

The acidity of the syrup is determined by measuring 10 ml. with a pipette and diluting this with about 30 ml. of distilled water. Into this N/10 caustic soda is run from a burette with constant stirring. The end point is determined with the aid of a few drops of phenolphthalein solution. The results are usually expressed as percentage of citric acid.

The sugar content of the syrup may be found sufficiently accurately for practical purposes by an estimation of the total soluble solids, using a refractometer in the manner previously described under canning syrups. There is no need in the present instance, of course, to cool the syrup by passage through the spiral condenser.

Determination of Cane and Invert Sugar.

In cases where it is desired to exercise a very complete control of the canning process, the determination of the proportion of "cane" and "invert" sugar present is carried out. The sweetening power and palate effect of the two sugars are by no means identical, and the proportion in which each is present is therefore not without its effect on the flavour of the product. But apart from this, inasmuch as when "cane" sugar is heated with fruit acids a portion of it is hydrolised into "invert" sugar (depending among other things upon time, temperature, and acid concentration), analytical

data on the amount of each sugar present gives valuable information on the conditions under which the test can be packed. This more complete determination of sugars is carried out by boiling with Fehling's solution, and experience has shown the general method devised by Lane and Eynon employing methylene blue as internal indicator gives satisfactory results.

With the syrup of most samples of canned fruit, it is convenient to take 10 ml. with a pipette and to make up to 500 ml. with distilled water. This solution is then titrated against 25 ml. of Fehling's solution in the standard manner, and gives the amount of "invert" sugar present.

For the determination of "cane" sugar,

an aliquot portion is withdrawn by pipette from the fruit syrup, and the whole of the sugar present converted to "invert" by heating under standard conditions with acid, and the solution so obtained is again titrated against Fehling's solution.

The figure obtained by the first titration subtracted from that obtained in the second, gives the amount of "cane" sugar present in terms of "invert" sugar, from which the original "cane" sugar is readily calculated.

A number of less important tests might be described, but these vary according to season, local canning conditions, and other factors, and in many cases should be obvious to any chemist in control of a given plant.

FISH CANNING

THE popularity of English canned fish is constantly increasing, and it is worthy of note that in addition to "Sild"—immature fish—and "Brisling," which is a two-year old sprat, the East Coast herring is beginning to be recognised as an important feature in the trade of this country.

The canning factory is capable of handling 500,000 fish per day and immediately the herrings are landed at the factory they are "roused" in the finest salt to harden the flesh, force out the blood and, finally, to impart flavour.

After remaining salted for approximately 18 hours each fish is "nobbled," i.e. the head is cut off and the guts drawn out, and then thoroughly washed in fresh water.

The headless and cleaned herrings are carefully selected, weighed, and placed in

the tins which are made from plate specially tinned and lacquered for that purpose.

Cooking Sterilization.

Mustard sauce or tomato purée of the finest quality is added, and the can is then automatically closed in a vacuum chamber after which the seams are examined, the tins washed and passed to the retort house for cooking and sterilization. Each retort is completely filled with trays on which are placed the filled cans and, after a preheating period, the cooking commences at a predetermined temperature for the appropriate length of time. This ensures complete sterility.

In due course the retorts are emptied; the cans are allowed to cool, after which they are examined, cleaned, and labelled ready for sale.

THE CHEMISTRY AND PHARMACY OF VEGETABLE DRUGS

PART XIII.—ALKALOIDAL DRUGS. 7. Ipecacuanha, etc.

By NOEL L. ALLPORT, A.I.C.,

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THE root of *Cephaelis Ipecacuanha* is a highly important drug, being at once an emetic, a diaphoretic, one of the most convenient of the known expectorants, and an excellent remedy for the treatment of amœbic dysentery. The root, which is derived from a small plant found in Brazil, especially in the province of Matto Grosso, occurs in commerce as dark brown, slender, tortuous, annulated rods about 15 cm. long and approximately 5 mm. in diameter (Fig. 1). Genuine ipecacuanha is also cultivated in the Straits Settlements. Cartagena ipecacuanha is an inferior variety grown in Colombia and frequently imported into this country; it may be distinguished by its larger size and the more widely separated annulations. Several substitutes for the genuine drug have from time to time been offered in the market, but, being devoid of the characteristic alkaloids, they are quite worthless (Fig. 2).

Chemistry of Ipecacuanha.

The root contains from 2 to 3 per cent. of total alkaloidal material consisting of

the three substances emetine, $C_{19}H_{40}O_4N_2$, cephæline, $C_{18}H_{36}O_4N_2$, and psychotrine. The alkaloids from genuine Brazilian or Indian (Johore) ipecacuanha consist of

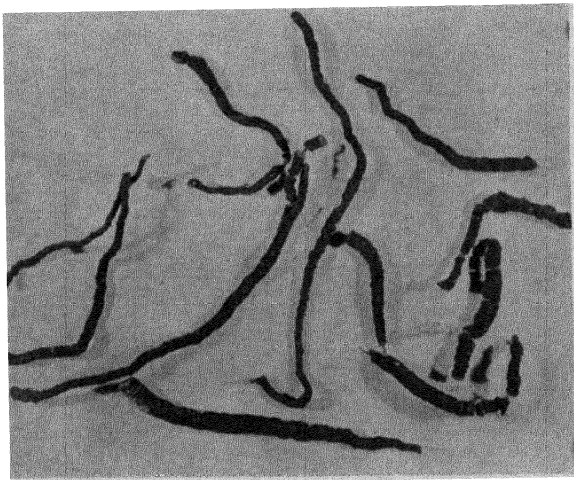


Fig. 1.—IPECACUANHA ROOT.

This shows a specimen of the typical Brazilian drug. It is imported in bales weighing about 1 cwt.

approximately 70 per cent. emetine and about 28 per cent. cephæline, while psychotrine constitutes the remainder. Cephæline is a phenolic body (containing the hydroxyl radicle OH) while emetine is the methyl derivative and is consequently non-phenolic. Although cephæline is a powerful emetic it is ineffective as an expector-

ant and its presence in excessive amount is undesirable. Cartagena ipecacuanha contains about the same proportion of total alkaloids as the Rio variety, but as only about 40 per cent. is emetine, it should not be employed for the preparation of galenicals.

Assay of Ipecacuanha.

The evaluation of this drug involves a determination of the total alkaloids and also the proportion of non-phenolic bases (mostly emetine). The following process is expeditious and reliable.

Determination of Total Alkaloids.

The root is powdered and 7 gm. treated

with 70 ml. of a mixture of chloroform 1 vol. and ether 3 vols. After 5 minutes, 5 ml. of 10 per cent. ammonia solution is added, the mixture shaken at intervals during one hour and the drug then agglomerated by the addition of about 5 ml. of water. 50 ml. of the clear supernatant liquid is transferred to a separating funnel and extracted by shaking with several portions of dilute hydrochloric acid. The mixed acid extracts are rendered alkaline with ammonia and the liberated alkaloids extracted with chloroform, each chloroformic extraction being washed in succession with about 10 ml. of water contained in a second separating funnel. The chloroform is removed by distillation, a little alcohol added and at once evaporated and the residue dried at 100° C. for 5 minutes. The alkaloidal residue is dissolved in an excess of decinormal sulphuric acid and the solution titrated back with decinormal sodium hydroxide using methyl red as indicator. Each ml. of decinormal acid is equivalent to 0.0240 gm. of total alkaloid, calculated as emetine.

Determination of Non-phenolic Alkaloids.

The above titration liquid is transferred to a separating funnel, rendered alkaline with sodium hydroxide solution and shaken with about 50 ml. of ether. The separated ethereal solution is agitated successively with two portions of very dilute aqueous sodium hydroxide, these alkaline shakings then added to the main aqueous solution and the mixed alkaline liquid extracted with further portions of ether. The mixed ethereal solutions are washed with successive quantities of about 10 ml. of water until free from alkali, each of the aqueous washings being shaken in turn with a single portion of ether contained in another separating funnel. All the

ethereal liquids are transferred to a flask, the ether evaporated, and the amount of alkaloidal residue determined by adding an excess of decinormal acid and titrating back with decinormal alkali using methyl red as indicator, the result being calculated to emetine.

This procedure effects a separation of the cephaeline, which, being phenolic, forms a salt with the sodium hydroxide, and is thus left in the aqueous liquor when the emetine is extracted with ether.

Assay of the Galenicals.

The liquid extract of ipecacuanha may be assayed by transferring 10 ml. to a separating funnel, acidifying with dilute mineral acid, removing non-alkaloidal

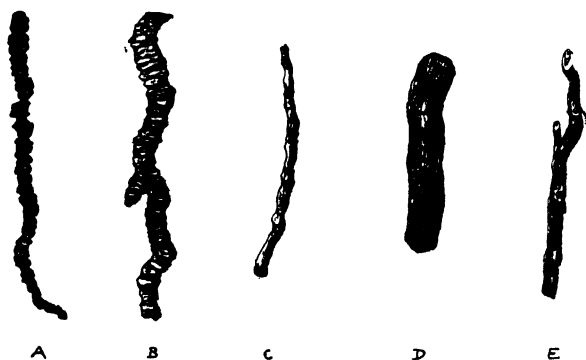


Fig. 2.—VARIETIES AND SUBSTITUTES FOR IPECACUANHA ROOT.

A, Genuine Brazilian root; B, Cartagena ipecacuanha; C, Undulated ipecacuanha (*Richardsonia* sp.); D, Lesser striated ipecacuanha (*Richardsonia* sp.); E, Greater striated ipecacuanha (*Psychotria emetica*). The three latter substitutes do not contain any emetine or cephaeline.

extractive matter by shaking with several portions of chloroform and, after rendering alkaline with ammonia, extracting the alkaloids with chloroform in the usual way and titrating the residue. The separation of the non-phenolic alkaloids is then conducted by treating the titration liquid

by the method already described. When dealing with the more dilute galenicals, larger volumes are taken and evaporated to low bulk before commencing the extraction.

The Pharmacy of Ipecacuanha.

Preparations made from the whole drug are particularly useful as expectorants in the treatment of bronchitis and whooping cough. The liquid extract, which is standardised to contain 2 per cent. of total alkaloids, is made by the standard percolation process with 90 per cent. alcohol (see Vol. I, page 42). It is used principally for making the weaker galenicals which are more suitable for prescribing.

Ipecacuanha Wine.

This consists of a 5 per cent. by volume solution of the liquid extract in sherry. This is then filtered after standing for 48 hours. It should contain 0.1 per cent. of total alkaloids, but, in practice, some alkaloidal material is carried down by the precipitate which forms when the liquid extract is mixed with the wine.

Tincture of Ipecacuanha.

In the present British Pharmacopœia the time-honoured ipecacuanha wine has been replaced by a tincture made by diluting 5 vols. of the liquid extract to 100 vols. with alcohol, glycerin and water; it contains about 22 per cent. of alcohol. The dose for the purpose of an expectorant is 10 to 30 minims, while, if a fluid ounce be administered, the preparation acts as an emetic in the course of about half an hour.

Vinegar of Ipecacuanha.

This preparation is considered by some physicians to be a more effective expectorant than the wine and is made by diluting 5 vols. of the liquid extract with 10 vols. of 90 per cent. alcohol and 85 vols. of 5 per cent. acetic acid.

Compound Powder of Ipecacuanha.

This is a useful diaphoretic for the treatment of colds and consists of 10 per cent. each of powdered ipecacuanha root and opium, with a suitable diluent such as potassium sulphate or lactose. It is known as Dover's Powder, after its originator, and many different formulæ for the preparation have been tried, but all contain ipecacuanha and opium as the essential ingredients.

Lozenge of Morphine and Ipecacuanha.

This preparation is an excellent remedy for severe coughs and is made by adding powdered ipecacuanha root and morphine hydrochloride to sucrose and gum acacia,

both in fine powder, adding a little tincture of tolu and making into a paste with water. After cutting, the lozenges are dried in a hot-air chamber. Each lozenge should contain $\frac{1}{10}$ of a grain of ipecacuanha and $\frac{1}{32}$ of a grain of morphine hydrochloride.

Treatment of Amoebic Dysentery.

There are two principal varieties of dysentery, that known as bacillary being due to the *Bacillus dysenteriae* (of Shiga or of Flexner), and the amoebic form caused by a protozoa called *Entamoeba histolytica* (Fig. 3). The latter disease, which is very common in all tropical countries, is well treated by ipecacuanha. The administra-

tion of the root itself is attended with difficulties owing to its emetic properties and it is now customary to give emetine hydrochloride by injection or to administer the insoluble emetine bismuth iodide orally.

Of the several species of parasitic amoebæ liable to inhabit the human intestines, *Entamoeba histolytica* is the only one which is pathogenic. Its diet consists

almost entirely of red blood corpuscles and it secretes a ferment capable of dissolving the mucous membrane of the large intestine, thus enabling it to reach the submucosa and then extend its excavations laterally beneath the surface, forming typical flask-shaped ulcers. During an acute attack of dysentery swarms of amoebæ can be found in the stools, which consist mainly of a purulent mixture of blood and mucus; the intestinal actions, accompanied by intense pain, often take place every few minutes. Treatment of this condition by emetine rapidly destroys the majority of the amoebæ, not only giving merciful relief to the patient but preventing almost inevitable death. The liability to further acute attacks generally remains, and it seems probable that a few of the organisms must manage to escape

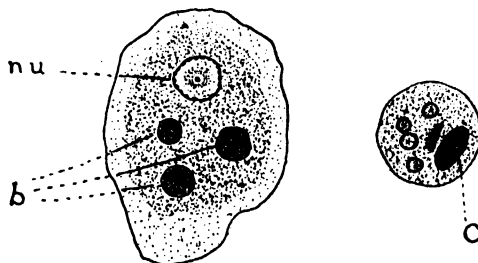


Fig. 3.—*ENTAMOEBA HISTOLYTICA*.

The protozoa responsible for amoebic dysentery, magnified over 1,000 diameters. The left-hand drawing shows the motile life stage; *nu*, the nucleus with peripheral chromatin granules and central karyosome; *b*, ingested red blood corpuscles. The right-hand drawing depicts the encysted non-motile life stage with four nuclei and the chromatoid body marked *C*. Before encystment, contained food is ejected.

the action of the drug, possibly by finding refuge in pockets of the intestinal walls.

Isolation of Emetine

The powdered ipacacuanha root is extracted with alcohol, the combined extracts acidified with hydrochloric acid, the alcohol distilled off and the residue diluted with water. The separated fat and non-alcoholic extractive material is filtered off, the filtrate rendered alkaline with ammonia and the alkaloids extracted with chloroform or ether. The cephaeline is removed by agitating the organic solution of the mixed alkaloids with aqueous sodium hydroxide, the emetine then extracted with hydrobromic acid and the emetine hydrobromide carefully recrystallised. The hydrochloride can be prepared by regenerating the base and, after separation, neutralising it with hydrochloric acid and recrystallising the salt.

The cephaeline separated by the sodium hydroxide solution may be converted to emetine by adding sodium bicarbonate to the alkaline liquid, extracting with chloroform, converting the base to its hydrochloride and purifying by recrystallisation. The cephaeline is then regenerated with sodium carbonate, extracted with chloroform, and the dried chloroformic extract of cephaeline alkaloid dissolved in a solution of sodium metal in fusel oil, sodium methyl sulphate added, and the cephaeline methylated by boiling the mixture under a reflux condenser. The resulting emetine is then extracted with diluted hydrochloric acid and purified by recrystallisation, any unchanged cephaeline being removed by treatment with sodium hydroxide.

Characteristics of Emetine and its Salts.

Emetine base occurs as an amorphous white powder which becomes yellow on storage. When a trace of emetine is

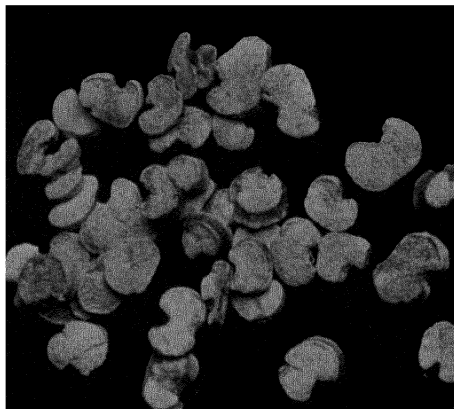


Fig. 4—COLCHICUM CORM

This is a specimen of material grown and prepared in England.

dissolved in a few drops of concentrated hydrochloric acid and a little hydrogen peroxide added to the solution, a deep yellowish-pink colour is produced. The hydrochloride ($C_{29}H_{40}O_4N_2 \cdot 2HCl \cdot 7H_2O$), is a colourless, odourless crystalline powder, readily soluble in water. If a small quantity of the hydrochloride is added to a very dilute solution of molybdic acid in concentrated sul-

phuric acid a bright green colour is produced. This reaction serves as an identity test.

Emetine bismuth iodide is a reddish-orange powder which is insoluble in water and alcohol, but is dissolved by acetone. Strong acids and alkaline solutions decompose the salt.

COLCHICUM.

The autumn crocus or meadow saffron (*Colchicum autumnale*) is used as a specific remedy for gout. The plant is distributed over Europe and is common in England. Both the dried corm and seeds are employed in the preparation of galenicals. The corm occurs in commerce cut into greyish-white slices about 3 mm thick and approximately 1.5 cm in diameter. The hard, dull, nearly spherical reddish-brown seeds are about 2.5 mm. in diameter. Both the dried corm and seeds are odourless, but have a bitter taste.

Chemistry of Colchicum.

The physiologically active constituent of colchicum is the pale yellow, amorphous, highly toxic alkaloid colchicine, $C_{22}H_{25}O_6N$, of which the corm contains from 0.2 to 0.6 per cent. and the seeds 0.2 to 0.8 per cent. Colchicine is soluble in water and in the common organic solvents. Its acid solutions do not yield any reaction with Mayer's reagent (potassiummercuric iodide solution), but a brown

precipitate is produced by a dilute solution of iodine in aqueous potassium iodide.

Assay of Colchicum.

Although colchicine is soluble in water it is still possible to extract it from alkaline aqueous solution by agitation with chloroform, since the alkaloid dissolves even more readily in the organic solvent. The following process is applicable to both the corm and seeds.

Fifteen gm. of the powdered drug is digested with 10 ml. of lead subacetate solution and 290 ml. of water at 60-70° C. under a reflux condenser. After 3 hours the mixture is filtered and 200 ml. of the filtrate treated with 0.75 gm. of dibasic sodium phosphate and shaken at frequent intervals during 30 minutes. The mixture is again filtered and 100 ml. of the filtrate (equivalent to 5 gm. of colchicum) transferred to a separating funnel and the alkaloid extracted by shaking with several portions of chloroform. In order to ascertain when extraction is complete a few drops of the chloroformic extract should be evaporated to dryness on a watch glass, any residue dissolved in a little dilute hydrochloric acid and the liquid tested for colchicine by adding a solution of iodine in aqueous potassium iodide; the presence of colchicine will be indicated by the formation of a brown precipitate.

When all the colchicine has been removed from the aqueous layer the chloroformic extract is transferred to a tared flask, the solvent distilled off, and the residue treated with 1 ml. of alcohol, the latter at once evaporated, more alcohol then added and evaporated off and the residue dried at 100° C. and weighed. The residue consists of colchicine and a trace of resin, the proportion of which is determined by adding 10 ml. of water,

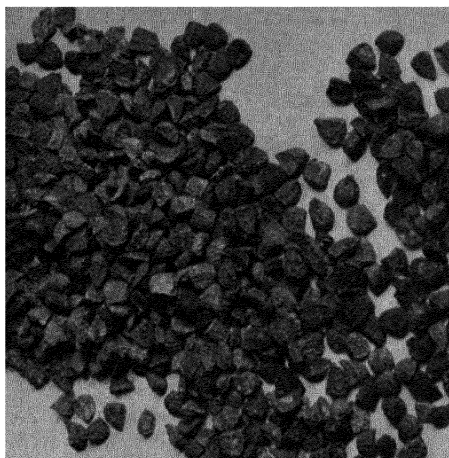


Fig. 5. STAVESACRE SEEDS.

Preparations of these poisonous seeds are employed for the destruction of lice. Their use has considerably declined since the introduction of modern coal-tar disinfectants and generally improved hygienic conditions.

filtering the resulting solution through a pledget of cotton wool, washing the wool free from colchicine, dissolving the water-insoluble resin in alcohol, evaporating to dryness in a tared dish and weighing after drying at 100° C. The weight of the resin deducted from the first weight gives the weight of colchicine in 5 gm. of the drug.



Pharmacy of Colchicum.

Colchicum relieves pain and inflammation due

to gout and is frequently prescribed in association with purgative drugs. Its continual use is liable to cause derangement of the central nervous system and it is necessary to exercise caution in its administration.

The dry extract, for use in pills, is made from the corm by the standard percolation process, using 60 per cent. alcohol. The percolate is evaporated under reduced pressure at a temperature not exceeding 60° C. and is standardised to contain 1 per cent. of colchicine.

The liquid extract, used for making tincture of colchicum, is prepared by the standard percolation method with 60 per cent. alcohol from the powdered and defatted seeds. It should contain 0.3 per cent. of colchicine. The tincture is made by diluting the liquid extract to ten times its volume with 60 per cent. alcohol, allowing to stand for at least 12 hours, and filtering.

Colchicum Wine.

This galenical is prepared by macerating 20 parts of the powdered corm with 100 parts of sherry for seven days, straining, pressing the marc, mixing the liquids obtained, and filtering. Colchicum wine is frequently prescribed with antacids and saline purgatives.

Colchicine and Tumours.

For some time an inter-relationship has been suspected between the action of colchicine and mitosis (indirect nuclear division) following on the discovery of mitotic figures in the hæmopoietic, or blood-making, organs of normal healthy animals, and also in the neoplastic tissues of tumours after the administration of colchicine. Preliminary experiments have very recently been conducted by E. C. Amoroso, of the Royal Veterinary College, London, which indicate that injections of colchicine are capable of effecting the dispersal of tumours, and it is announced that further work in the treatment of these maladies with colchicine in association with X-rays and with radium is now being actively pursued.

STAVESACRE.

Preparations made from the seeds of *Delphinium Staphisagria*, a herb indigenous to Asia Minor and Southern Europe, were once extensively employed for the destruction of head lice and their ova. The odourless seeds are obscurely quadrangular or triangular in shape, and measure approximately 6 mm. in length, while the outer coat is characterised by a reticulated and pitted surface.

The drug contains several alkaloids, amounting altogether to about 1 per cent. Of these the most important are delphinine, $C_{31}H_{49}O_7N$, delphisine and delphinoidine. Delphinine and delphisine are intensely toxic. Stavesacre ointment is made by digesting the crushed seeds with benzoated lard on a water-bath and stiffening the resulting preparation by the addition of beeswax. Stavesacre lotion is made by treating the powdered seeds with boiling dilute acetic acid and, after cooling, adding a dilute alcoholic solution of the oils of geranium, lavender and lemon, and finally diluting with glycerin and water.

Owing to the improved hygienic facilities of modern times, remedies for the destruction of head lice are in less demand and, even when required, safer methods are now available, such as treatment with kerosene emulsion or preparations of naphthalene.

Summing up the relative values of the three drugs just discussed, it may be said that stavesacre is almost obsolete; that ipecacuanha is a heaven-sent remedy for innumerable victims of dysentery; and colchicum, although at present only employed to alleviate one disease, has possible potentialities that may cause it to become a drug of primary importance.

REFRACTOMETERS FOR TESTING JAMS, ETC.

THE refractometer generally used in the sugar and confectionery trades is a modification of the old butyro or butter refractometer. This instrument can be used for testing all fats, oils, sugars and jams, that is solutions which have their refractive index between 1.42 and 1.49. The instrument consists mainly of two prisms, one polished and the other one greyed, which are housed in a metal box, and a constant flow of water at a definite temperature is passed round them. A telescope is placed on the prism box and a border line is obtained in the eyepiece. Looking into the eyepiece one sees a scale divided from 0-105 on the upper divisions

and a sugar per cent. scale on the lower reading from 0-50. The upper scale, which is the standard butter scale, is divided into tenths by the aid of a micrometer drum.

These are the refractometer numbers referred to in the standard text books on oils and fats.

The lower scale gives the percentage soluble solids of sugar solutions, and in the latest type of instrument made by Bellingham & Stanley a temperature correction drum has been added which obviates the use of tables and gives a corrected reading in the eyepiece, thus saving much time.

PAINTS AND VARNISHES

PART VI.—LEATHER FINISHES

By H. COURTNEY BRYSON

LEATHER finishes are conveniently divided into (a) unpigmented finishes and (b) pigmented finishes, which are of quite recent origin, having been originated during the war because of the shortage of dyestuffs. Unpigmented finishes are generally used as seasonings, i.e., dilute solutions applied to the grain side, leaving a thin flexible film sufficiently hard to take a polish when the leather is glazed by rubbing mechanically, e.g., with glass or agate. Albumen is one of the chief components and its use for this purpose dates back to the time of the Pharaohs.

Albumen.

Egg albumen is used particularly for light coloured leather, and a typical plain seasoning contains 1.5 per cent. egg albumen, 4.5 per cent. milk made up to 100 with water. The film on prolonged exposure becomes insoluble. Insolubility may be conferred immediately by the application of heat, e.g., ironing the skin, or by treatment with a dilute solution of a metallic salt which will not react with the tannin of the leather. The chief test performed on egg albumen is for insoluble matter.

Blood albumen is used for dark coloured skins and a typical seasoning consists of 15 per cent. of this albumen with 1 per cent. of a water soluble nigrosine black and $\frac{1}{2}$ per cent. glycerine, combined with 10 per cent. milk and made up to 100 with water. Milk is a favourite constituent of seasoning mixtures since it contains 3 per cent. of dispersed casein as well as 3 per cent. of butter fat in emulsion which acts as a lubricant when the leather is being glazed.

Lactic casein is best treated by Mummery and Bishop's test (see page 1312). It is

only soluble in water containing bases or basic salts which convert it into a sticky solution of the particular salt employed. It is not coagulated by heat and is only precipitated by certain metallic salts, though it may be rendered insoluble by formaldehyde. An excellent seasoning may be prepared by dissolving 2 per cent. of casein in 10 per cent. of whole milk with the aid of .35 per cent. of borax. The higher the amount of borax present the longer will the solution keep without the aid of preservatives but the quicker will it lose viscosity. Formaldehyde is a favourite "fixative" for casein and it may be added direct under rigorously controlled conditions to a casein solution, thus eliminating a subsequent operation.

Precautions When Using Lactic Casein.

Solutions of lactic casein will set to a gel when formalin is added unless the following precautions are observed:—

- (1) Free alkali must not be present. In other words, the pH value of the solution must not be over 6.5.
- (2) Neither solution must be hot.
- (3) The formaldehyde solution must not be more concentrated than 10 per cent., nor the casein of a greater strength than 12 per cent.
- (4) The addition of the formalin must be made slowly with constant stirring in a thin stream.

Other Components.

Glue, gelatine and Irish moss are also employed, the first two giving brittle films, though they are valuable as an economiser in staining or flaming and topping leather to prevent penetration and wastage of dyestuff. Shellac in the form of a soap made by dissolving the resin in aqueous solutions of borax or ammonia

though it tends to give a harsh film is very largely used in pigmented finishes as it readily wets leather and gives good penetration so that the finish is well anchored to the skin.

It should be noted that the solubility of shellac decreases about 5 per cent. per annum, therefore, the older the specimen the greater the quantity of alkali needed to effect solution.

Wax, when emulsified and dispersed, usually by boiling up with soap solution, serves several valuable purposes, especially in pigmented finishes, since it tends to give an excellent finish under the brush and seals the pores of the skin, so decreasing penetration in very open leathers and thus aids spreading power.

The Plasticiser.

In addition to the above substances, scarcely any of which of themselves dry out to produce a continuous film, it is necessary to incorporate a small quantity of plasticiser. Almost any inert, non-drying water-soluble organic colloid can act as softening agent or plasticiser. Sulphonated oils such as turkey red oil or sulphonated cod oil and the like are consequently frequent constituents of leather finishes. They also confer a better "feel" or "handle" to the skins. Turkey red oils may be manufactured by adding concentrated sulphuric acid to second pressing castor oil, allowing to stand, washing out the excess acid with saturated salt solution and neutralising with ammonia or caustic soda to such a degree as to be either acid, neutral or alkaline, the latter being the most commonly desired state. Whether

made or bought, all batches should be tested for pH value and water content.

Attempts to use latex as a leather finish have so far proved abortive since it does not possess a "kind" feel and the size of the globules are larger than the diameter of the capillary fibres in the skin, consequently the film may be peeled from the surface after drying.

The Pigments.

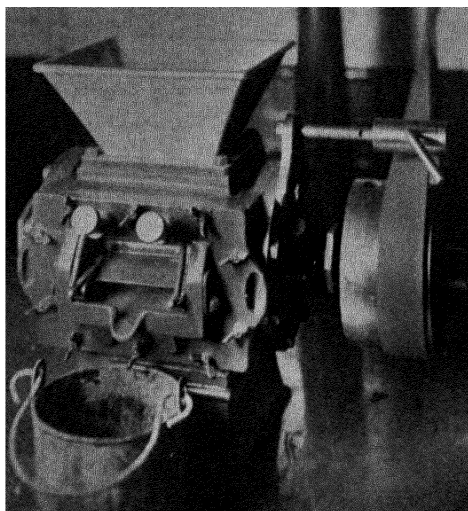
The pigments used in leather finishes

must be very finely ground—far more finely than is usual with the ordinary type of paint pigment. Oxides and ochres are the commonest pigments employed, and, in general, English oxides are to be preferred. There has recently become available a new synthetic oxide which is so fine that 90 per cent will pass through a 1,000 mesh sieve and this is ideal for this type of finish. Coarse particles must be entirely eliminated as these form centres from which cracking will occur when the leather is stretched or creased. The texture of the pigment must be smooth and soft. Harsh pigments will not adhere to the skin, coming off

easily with either wet or dry rubbing. Lead must be absent and the pigment must resist sulphuretted hydrogen. Lakes are used to get the more brilliant colours, but they are naturally deficient in hiding power.

Selection of Pigments.

The selection of pure fine pigments is one of the greatest difficulties encountered in the manufacture of leather finishes. Many pigments cause coagulation, gelatinisation or precipitation of the medium.



Borough Polytechnic
FIG. 1.—AN EXPERIMENTAL SINGLE ROLL PAINT MILL USED FOR STRAINING LEATHER FINISHING SOLUTIONS

A bar adjusted by the two milled screw heads presses against a revolving steel cylinder (driven by the pulley), which feeds a thin film of paint, contained in the hopper, through the gap between it and the bar, the film being removed continuously by the scraper. Coarse particles cannot get through the gap and are retained in the hopper.

For instance, if a negatively charged pigment be added to a negatively charged colloidal sol then coagulation will probably result. As an example, certain ochres are not readily wetted by egg albumen. If, however, they are evenly distributed throughout the medium they cause a gradually thickening till the whole assumes the appearance of a solid gel. The disastrous effects associated with flocculation have been discussed in the section on paints.

Plant.

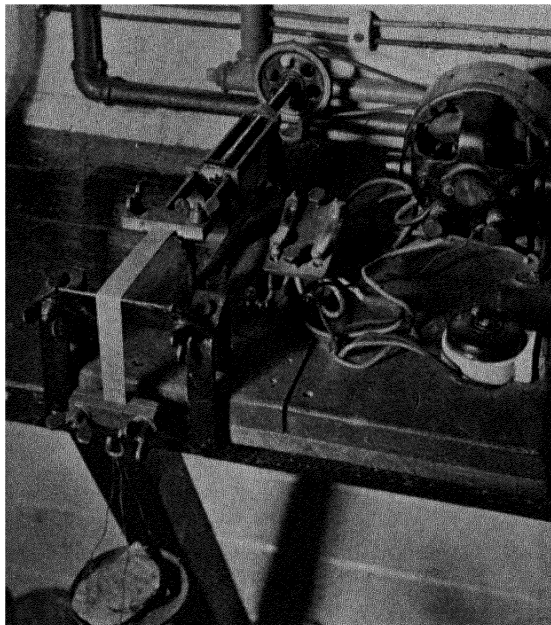
The importance of the grinding has already been stressed. The optimum size for the particles of the earth pigments is probably of the order of .0002 in. and a common procedure for producing this result is as follows: The whole of the pigment and the plasticiser and that part of the medium which does not contain any bodies convertible or coagulated by heat or shearing stress are mixed in a whisk or some type of fast mixing machine. The mixture is then fed into finely-set cone mills, which in turn feed flat stone burr mills, two cone mills feeding one burr mill. The former mills not only give a preliminary grind but act as a reservoir for the latter.

The Albumens are now Added.

After the grinding is finished the albumens and the like, which would have been coagulated either by the heat developed in grinding or the shearing stresses of the mills, are added and the batches are put into stock. It is usual to make up about a dozen or so stock

colours and to produce all the intermediate secondary and tertiary colours by suitable blends of the stock colours.

The proportion of pigment to binder in the finished product is usually rather high, e.g., about one to two. In general, materials rich in binder tend to give a film which is darker in colour than when in the wet condition, and vice versa. A proportion of about 1:2 represents the transition point with minimum change in colour value.



Paint Research Station
Fig. 2.—MACHINE FOR TESTING THE FLEXIBILITY OF LEATHER FINISHES.

Flexibility of Leather Finishes.

A good pigmented leather finish should be sufficiently flexible not to crack or craze when the leather is stretched or bent. Flexibility must always be considered in relationship to the surface of which the material is applied. Different surfaces and different modes of application with the same material will give very different results when tested for flexibility. On absorbent surfaces the

most flexible finishes will crack or peel off if the surface tension and the viscosity of the solution are not correctly adjusted.

How Comparative Flexibility is Tested.

Comparative flexibility is tested by the device shown in Fig. 2. A strip of leather is gripped between two jaws and then bent at right angles over an edge. A weight is suspended from the lower jaw. A motor actuates a worm which slowly causes the upper jaw to recede, dragging the leather strip over the edge in the process. At the end of the length of travel a trip drops on the commutator shown right in the middle

of the picture, causing the mercury contained in the glass tubes to flow to the other end, which reverses the motor, and the upper jaw changes its direction and moves forward, the weight on the lower jaw keeping the leather taut the whole time. The specimen thus undergoes a constant to and fro or see-saw motion over the edge and is inspected at intervals till cracking is apparent. The tension on the strip is altered by adjusting the weights.

Other Characteristics.

In addition to the above property of flexibility, the finish should possess the following characteristics:—

(a) It should not seal the leather completely with an impervious film as this would prevent the leather from "breathing," which is one of its most valuable characteristics, especially important in such objects as shoes.

(b) It should not be subject to changes in viscosity or surface tension under the action of time or temperature variations.

(c) It should be capable of resisting putrefaction for long periods, even in hot weather.

(d) It should be possible to add small quantities of acid or basic dyestuff to it without disturbing its balance. This in order to stain and pigment in one operation or for the purposes of tinting.

(e) It should possess good hiding and spreading power or it will not be economical in use.

(f) There must be sufficient lubricant (e.g., wax) present to inhibit scorching or tearing should it be desired to glaze under a mechanically applied agate.

(g) It should be reasonably fast to wet and dry rubbing.

(h) It should be substantially neutral.

(j) It must penetrate the leather slightly but not too much or the pigment will be left deficient in medium and powder off.

(k) When dry it should leave the leather soft and supple and not stiff or harsh.

How Leather is Finished.

A typical example of the method of finishing leather is as follows:—

The skin is bottomed with a basic dyestuff in aqueous solution (about $\frac{1}{2}$ per cent. concentration), plus a little acetic acid and possibly some alcohol if the skin is greasy. The acetic acid is added to the water first. If the grain is very open a preliminary sizing may be given with Irish moss. This is followed by the application of a coat of pigmented finish. The skin is sometimes very lightly buffed in order to form a good key. The finish, which is diluted with special thinners which consist essentially of an aqueous solution of the same binding media used in the finish itself, is applied manually by means of a seasoning brush, the aim of the worker being to produce a fine even coat and to preserve as much as possible the natural appearance of the skin. The commonest fault is to apply too heavy a coat or too concentrated a solution so that the natural beauty of the skin is hidden and the leather looks painted.

A second coat of pigmented finish is then applied after the first is dry by means of a spray pistol, taking the same precautions.

Finally, two coats of clear medium are applied to the leather in exactly the same way. The thinners, which provide additional binding medium, and the top coat or coats of clear finish serve to compensate for excess of pigment in the original pigmented solution. If the whole process is skilfully carried out it is almost impossible to tell that the leather has been painted. In fact by this modern method of treatment clear level shades may be produced from skins which in days gone by would have appeared streaked and patched, due to uneven dyeing.

CHEMISTRY IN THE STUDY OF DISEASE

PART II.—ANALYSIS OF URINE

By SIDNEY L. TOMPSETT, Ph.D.(Glas.), B.Sc.(Lond.), A.I.C.

VERY valuable information may be obtained from a chemical examination of the urine, and always precedes that of any other body fluids or excreta. The examination of the urine is included in the routine examination of every patient entering hospital. Often the detection of an abnormal substance in the urine is the first indication of organic disease, especially in their early stages when they are more amenable to treatment, e.g., protein, blood in renal disease, glucose in diabetes mellitus.

Composition of Urine.

Normal urine has approximately the following composition. It varies considerably with diet.

	<i>Per diem.</i>
Volume	1,000-1,500 ml.
Total nitrogen	10-15 gm.
Urea	20-30 gm.
Total sulphur	0.5 gm.
Phosphorus (chiefly in the form of inorganic phosphates)	1 gm.
Uric acid	0.5 gm.
Chlorides (chiefly as sodium chloride)	10-15 gm.

Also creatinine and potassium, calcium and magnesium as salts. From 75 to 90 per cent. of the sulphur is present as inorganic sulphates, the remainder being in the form of ethereal sulphates and organic sulphur.

TESTS FOR ABNORMAL SUBSTANCES IN URINE.

Protein, Proteose and Bence-Jone's Protein.

To 20 ml. of urine, add 1 ml. of 33 per cent. acetic acid and filter. The filtrate should show a strongly acid reaction towards litmus. This procedure is necessary to remove mucus, which is present

in normal urine in small amounts and in large amounts in certain catarrhal conditions of the bladder. Its presence is of no significance but it may be confused with proteins of significance.

To 5 ml. of the above filtrate is added 1 ml. of 20 per cent. salicylsulphonic acid. If a white precipitate is formed, the mixture is heated to boiling. A white precipitate which is insoluble on boiling indicates the presence of protein. A white precipitate which dissolves on heating to reappear on cooling will indicate the presence of proteose or Bence-Jone's protein. These two latter may be distinguished by means of the following test :—

5 ml. of the acid urine filtrate is heated in a water bath, the temperature being noted carefully with a thermometer. Bence-Jone's protein gives a precipitate at 40°-50° C., reaching a maximum at 70° C. This precipitate redissolves on raising the temperature to 100° C. but reappears on cooling. Proteose gives no precipitate with this test. *Note.*—Protein also gives a precipitate but it is not affected by boiling.

Blood.

To 5 ml. of urine in a test tube, add a few drops of saturated solution of guaiacum in absolute alcohol, followed by about 1 ml. of hydrogen peroxide (10 vol.). A blue colour suggests the presence of blood, but certain other substances, e.g., iodides (taken as a drug), certain enzymes, etc., also give a similar colour with this test. In the event of a positive reaction, the presence of blood must be confirmed by the following modification of the test :—

To 10 ml. of urine in a test tube, is added 1 ml. of glacial acetic acid and the mixture heated to boiling. The mixture after thorough cooling is shaken with about 5 ml. of ether. After separating, the ether layer is removed and tested with

guaiacum and hydrogen peroxide as described above. A blue colour indicates a positive reaction.

Bile Pigment.

To 5 ml. of fuming nitric acid in a test tube, add carefully without mixing 5 ml. of urine. A green or blue ring at the junction of the two fluids indicates the presence of bile pigment (bilirubin).

Bile Salts.

Sprinkle the surface of the urine in a test tube with some flowers of sulphur. The particles will sink to the bottom of the tube if bile salts are present. Compare with a normal urine. Bile salts if present reduce the surface tension of the urine which causes the flowers of sulphur to sink instead of floating on the surface.

Urobilin.

Place about 10 ml. of urine in a test tube, acidify it with a few drops of glacial acetic acid and extract the mixture with 5 ml. of amyl alcohol. Remove the amyl alcohol layer and add to it a few drops of a saturated alcoholic solution of zinc acetate. A green fluorescence indicates the presence of urobilin.

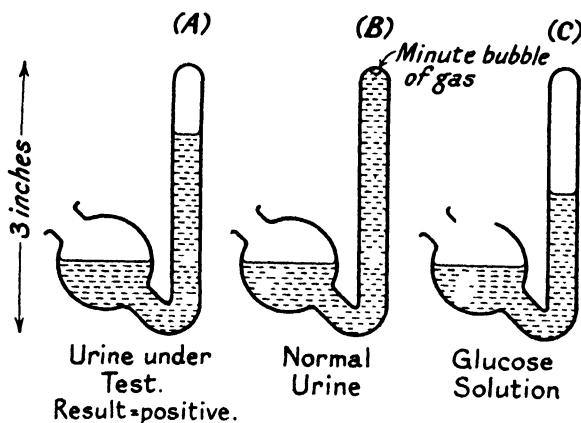


Fig 1 —THE FERMENTATION TEST

ACETONE BODIES.

(a) Rothera's Test.

To about 5 gm. of solid ammonium sulphate in a test tube, add 10-15 ml. of urine, then a few drops of freshly prepared sodium nitroprusside solution and finally 2-3 ml. of concentrated ammonia. Shake well and allow to stand. The development of a permanganate colour indicates the presence of acetone bodies.

(b) Gerhardt's Test.

To 5 ml. of urine add 10 per cent. ferric chloride solution drop by drop until

no further precipitation of phosphates occur. A cherry red colour indicates the presence of acetoacetic acid.

Acetoacetic acid gives both of these tests, whereas acetone gives only the Rothera test. Acetone often occurs alone in urine, but acetoacetic acid is never found unless acetone is present.

Salicylates appear in the urine after their administration. The administration of aspirin also results in the appearance of salicylates in the urine. Salicylic acid gives a purple colour with ferric chloride, which should not be confused with the colour given by acetoacetic acid. After its administration, phenazone appears in the urine and gives a Bordeaux red colour with ferric chloride. When

these substances are present in urine it is impossible to detect acetoacetic acid by the ferric chloride test, but the Rothera test is not interfered with.

Reducing Substances.

To 5 ml. of Benedict's qualitative reagent in a test tube is added

exactly 8 drops of urine. Place in a boiling water bath for 8 minutes. A green, yellow or red precipitate of cuprous oxide indicates the presence of "reducing substances."

Benedict's qualitative reagent has the following composition —

173 gm. sodium citrate, 100 gm. anhydrous sodium carbonate, 17.3 gm. crystalline cupric sulphate in 1,000 ml. distilled water.

The following substances which may be present in urine, reduce Benedict's reagent: glucose, lactose, pentose sugars, conjugated glycuronates and homogentistic acid. The nature of the reducing substance may be determined by the following tests:—

(a) Fermentation Test.

Of the above substances, glucose is

the only one that is fermented by yeast with the production of carbon dioxide.

Some baker's yeast is made into a suspension with distilled water and filtered through some fine muslin. This is very important as yeast often contains sugars and other fermentable substances.

The urine under test is then boiled to destroy organisms.

Three fermentation tubes, similar to that shown in the diagram, are labelled (a), (b), and (c) respectively, and a piece of washed yeast added to each. These tubes are now filled as follows :—

- (a) The urine under test ;
- (b) Normal urine ;
- (c) A 1 per cent. solution of glucose.

These three tubes are now placed in an incubator at 37° C. for 24 hours. At the end of 24 hours,

(c) Should show a large volume of gas, indicating that the yeast is working well.

(b) Should show no gas, indicating that the yeast has been washed properly.

(a) If a gas has been formed, the reducing substance must be glucose.

(b) Osazone Test.

Of the above reducing substances, glucose and lactose form osazones which have a characteristic crystalline form.

To 10 ml. of urine in a test tube, add 1 ml. glacial acetic acid, 1 gm. phenylhydrazine hydrochloride and 2 gm. sodium acetate. Mix thoroughly and place in a boiling water bath for 1 hour. Then allow the tube to cool slowly in the water bath to room temperature. Examine a little of the solution under the microscope for crystals of glucosazone or lactosazone.

The osazones are canary yellow in colour. Glucosazone is very insoluble in hot water and separates readily even when the solution is hot. Lactosazone on the other hand is soluble in hot water and does not crystallise out until the solution is cold.

(c) Tollen's Test.

This test will detect the presence of pentoses and glycuronates.

To 5 ml. of urine in a test tube add an equal volume of concentrated hydrochloric acid and a knife point of phloroglucin. Place in boiling water bath and watch carefully. The development of a cherry red colour indicates the presence of glycuronates or pentoses.

(d) Bial's Test.

This test will detect the presence of pentoses.

The reagent is prepared by dissolving 1 gm. of orcin in 500 ml. of concentrated hydrochloric acid and then adding 25 drops of 10 per cent. ferric chloride.

To 5 parts of Bial's reagent add 1 part of urine and bring just to the boil. Pentoses give a green colour and sometimes a bluish-green precipitate.

The presence of homogentistic acid may be confirmed by the following tests :—

On standing, or on the addition of alkali, the urine will turn brown to brownish-black.

The addition to the urine of ferric chloride solution, drop by drop, will result in the formation of a blue colour.

INTERPRETATION OF RESULTS.

The presence of either protein or blood in the urine is suggestive of disease of the kidney. The protein is a mixture of albumin and globulin, usually chiefly the former. The protein is a result of a leakage of blood plasma through the glomeruli, owing to their diseased condition. In such a condition the blood corpuscles do not pass into the urine and since the "test for blood" is due to the presence of hæmoglobin, the urine will yield a negative test for blood. In some conditions there is a hæmorrhage or bleeding in the renal tract due to inflammation. This will result in a urine with a red colour. In such a condition the urine will contain red blood cells and consequently hæmoglobin, and will give a positive test for blood. Often the presence of these substances in the urine are the first indications of kidney disease.

Presence of Proteoses.

The presence of proteoses in urine are not of diagnostic importance and are found in the following conditions—pneumonia, diphtheria, cancer, dermatitis, etc. It is important not to confuse them with protein.

Bence-Jones's protein is important since its presence in urine is considered to be diagnostic of certain malignant diseases of bone. This protein is distinct from any of those present in blood and tissues, in fact, its origin is very obscure.

Bile Pigment and Bile Salt.

Bile pigment and bile salts are found in

the urine in any condition in which the flow of bile from the liver into the intestine is obstructed. Urobilin is found in the urine in conditions in which there is an excessive destruction of red blood cells, e.g., due to a toxic agent, or in those conditions in which the liver cells are damaged. When the liver cells are very severely damaged, bile pigment as well as urobilin may be present in the urine. Many chemical substances, e.g., lead, arsenic, picric acid, etc., cause excessive

breakdown of the red blood cells and/or poison the liver and cause the excretion of bile pigment and urobilin in the urine. These will be dealt with in detail later.

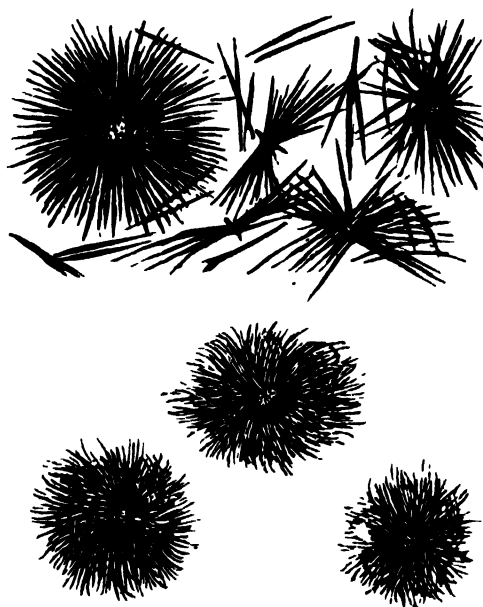
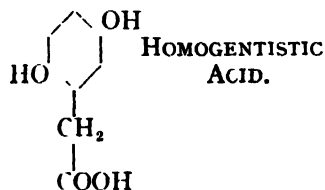
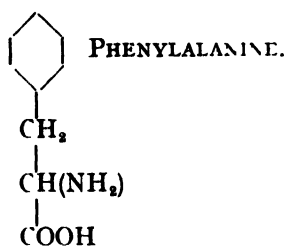
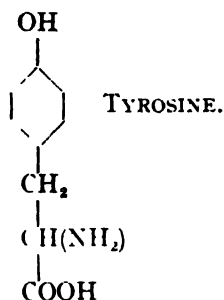


Fig. 2—OSAZONES.
Upper form, dextrosazone; lower form, lactosazone

etc., e.g., acetamide, phenazone, amidopyrin, camphor, chloroform, chloral, morphine, menthol, naphthol, phenol, thymol, oil of turpentine, etc., and in carbolic acid and lysol poisoning. The occurrence of pentoses in the urine is an abnormality peculiar to certain people and is associated with no ill effects. The occurrence of homogentistic acid is another abnormality peculiar to certain people, and is associated with no ill effects. It appears to be due to an inability to

completely metabolise the tyrosine and phenylalanine of the diet. The relationship between these substances will be seen from their formulae



Acetone Bodies.

Acetone bodies are found in the urine in severe cases of diabetes mellitus (sugar diabetes) and sometimes in starvation and excessive vomiting.

Reducing Substances.

Of the reducing substances that may be found in urine, glucose only is of any significance. Lactose is found sometimes in the urine of pregnant and lactating women. Glycuronates are often present in the urine after administration of many drugs,

What the Presence of Glucose Suggests.

The presence of glucose in the urine is suggestive of diabetes mellitus (sugar diabetes). Diabetes mellitus is a result of an inhibition of secretion of insulin by the pancreas, so that the oxidation of glucose in the tissues is reduced. This results in the accumulation of glucose in the blood and its appearance in the urine. In severe cases of this disease, the urine may contain anything up to 5-10 per cent. of glucose. Glucose is sometimes found in the urine as a result of "leakage through the kidney." This condition, known as

renal diabetes or renal glycosuria is not a serious one and requires no treatment. These two conditions may be distinguished by an examination of the concentration of sugar in the blood during fasting and after the ingestion of 50 gm. of glucose. In the former, the concentration of sugar in the blood is not abnormally high fasting, will be after the glucose. In the latter condition the blood sugar will be within normal limits, both during fasting and after the ingestion of glucose. It is very important from the patient's point of view to distinguish properly between these two conditions. He or she may be saved much needless discomfort.

The Colour of Urine.

Urine is normally amber in colour. Abnormal constituents, as a result of disease, may convey characteristic colours to the urine. These are shown in the following table:—

<i>Abnormal Constituent.</i>	<i>Colour of Urine.</i>
Blood	Red.
Bile Pigment . .	Greenish.
Urobilin	Orange.
Homogentistic Acid.	Brownish-black (after standing).
*Methæmoglobin	Dark brown.
*Hæmatoporphyrin.	Port Wine.

*These two pigments are derivatives of hæmoglobin and will be referred to later.

Effect of Drugs on Colour of Urine.

The ingestion of certain drugs, etc., produce characteristically coloured urines. These are illustrated in the following table.

<i>Drug, etc.</i>	<i>Colour of Urine.</i>
Beetroot	Orange pink, turning yellow on standing or on the addition of alkali.
Rhubarb	Normal, turning reddish orange on standing or on addition of alkali.
Phenolphthalein (e.g. purgen).	Normal, turning red on standing or on the addition of alkali.
Santonin	Greenish, turning pink on the addition of alkali.
Methylene blue (e.g. de Witt's pills).	Greenish blue.
Phenazone	Sometimes red.
Guaiacum (e.g. Eade's pills).	Green.
Aniline dyes (e.g. sweets).	Red.
Carbolic Acid and Lysol Poisoning.	Greenish or brownish black.

VACUUM OVENS

VACUUM ovens are usually tubular in shape, with screw-on on front door to withstand atmosphere pressure. They are heated by an external water jacket which is in turn heated by either gas flame or electric elements. Suitable vacuum gauge and fittings are arranged so that when connected to a vacuum pump the air can be drawn out of the oven until a vacuum inside is obtained.

This type of oven is becoming more

generally used, as with them it is possible to carry out moisture determinations in considerably less time than with ordinary ovens.

Higher results are given with vacuum ovens, and this is probably due to the fact that the actual amount of water driven off from the samples, at a certain temperature, may be rather more under vacuum conditions than under *ordinary* air heating at the same temperature.

IDENTIFYING AN UNKNOWN FOOD SUBSTANCE

By E. CROSS

THE food chemist is, in the majority of cases, a specialist. His work is confined to definite categories of food—sugar, milk, meat or cereals. Within his category he works out a scheme or routine which covers his ground.

Yet he is always liable to come up against something which does not normally come within his scheme. He may be presented with a tin, a jar or a bottle and be asked for an analysis of its contents and also to be able to duplicate its contents.

How does he tackle the job?

Primarily an analysis must be made, an analysis sufficiently complete to serve his purpose. Now the textbooks on food analysis are legion. There are scores of authoritative volumes on each category of food. It is impossible to be familiar with them all. Time is an important consideration too and the chemist cannot afford to digest all the theories and methods relating to each and every class of food. He has to get on with the job, to get definite and concrete results. Methods which give a reasonable degree of accuracy will serve his purpose. He must remember that he is not making a minute research nor accumulating data for a thesis.

Beyond the necessary extent of the analysis there are other boundaries to his work which he must bear in mind. He is dealing with food. There are, in the world, only a certain number of things which come under the heading of "food." His attention is confined to these things. But even this loose classification is further restricted. There are many things used for food over the world but the use of them all *commercially* is not possible. There are considerations of expense, rarity and keeping quality to be kept in mind. Again the laws relating to the manufacture and sale of foodstuffs draws the boundaries of his attention a little closer.

The Purpose of Food.

Food serves a definite purpose, that of nourishment. It must be capable of assimilation by the human organism. The human organism is not nourished by anything of the inorganic or mineral world beyond some few cases of inorganic substances, sometimes combined with the organic, which act as auxiliaries to nutrition, stimulants to digestion and appetite such as certain chlorides and phosphates. Of these the only one which ever occurs in any appreciable quantity is sodium chloride.

Food maintains life and comes essentially from life, from the vegetable and animal kingdoms.

The Constituents of Food.

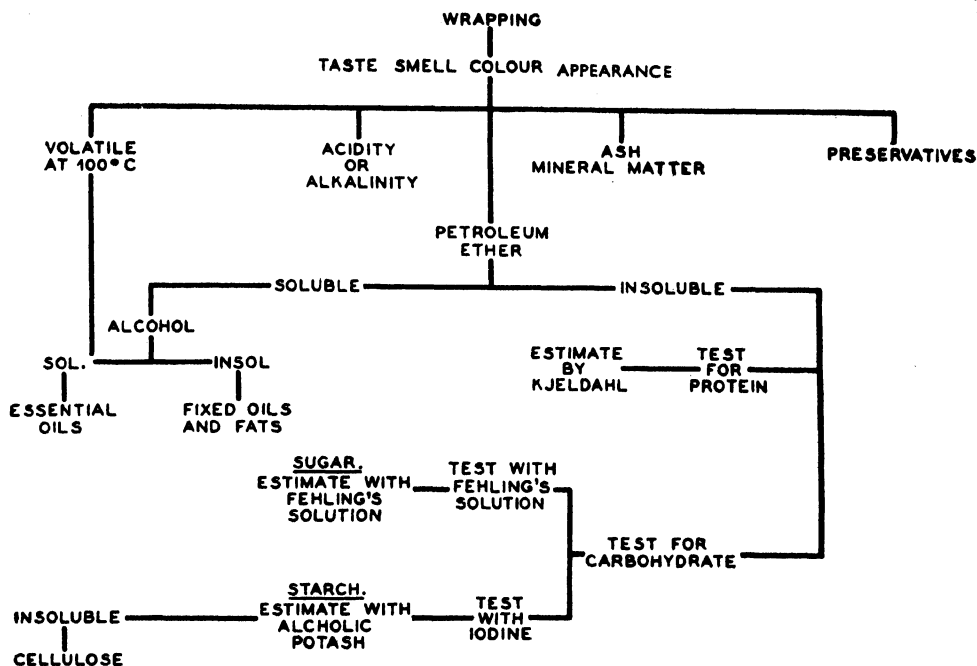
The constituents of food can be entirely classified into :—

Inorganic	..	Mineral salts
Organic	..	Fats and oils.
		Organic acids.
		Carbohydrates.
		Proteins.
		Cellulose.
		Flavouring materials.
Indifferent	..	Colouring materials.
		Preservatives.

Examine the Sample or Wrapping for Clues.

Before the actual chemical analysis the chemist must keep his eyes open for "clues" in the sample itself or the wrapping of it. The wording of the wrapper, its claims and instructions for preparation may give immediately an indication of the type of constituent which it is likely to contain to the man who uses his imagination in conjunction with his technical knowledge.

But there is the case where the sample may be wrapperless or there may be a mass of detail printed in Japanese, and



SUMMARY OF TESTS ON AN UNKNOWN FOOD SUBSTANCE.

even a works chemist is not expected to be familiar with Japanese. There is only the sample itself left.

Appearance, Taste and Smell.

The next approach is a physical examination of the sample.

Colour. (Natural or added.)

The range of colours used in foods is limited. Other than natural colour those colours which are added are usually suggestive of the constituents of the food or at least of one of the constituents.

Brown suggests cocoa, malt, or meat extract.

Golden brown suggests cereals.

Yellow suggests cereals, or eggs in some form.

Red suggests meat, or tomato.

Taste.

By taste the chemist looks for any pre-dominant flavour.

Salt.

Acid suggesting fruit.

Acid such as acetic.

Essential oils and esters suggesting fruit.

Sugar.

The bland taste of fats and oils.

The astringent taste of yeast extract.

Any distinctive taste such as cocoa or coffee.

Appearance.

Consider, particularly from the point of view of analysis, whether the sample is a paste, solid or liquid.

Smell.

The sharp, pungent smell of vinegar (acetic acid).

The burnt smell of caramel.

The warm smell of malt.

Cocoa. Coffee.

The above are some suggestions. The food chemist must familiarise himself at every opportunity with the distinctive characteristic of foods.

PRIMARY QUALITATIVE ANALYSIS.

Before the quantitative analysis a primary qualitative analysis into the various chemical groups of food must be made.

Group 1. Volatile at 100°C. Moisture, alcohol, essential oils, acetic acid.

Group 2. Mineral matter.

Group 3. Soluble in petroleum ether. Fats, oils, alkaloids, lecithin.

TABLE SHOWING CLASSIFICATION OF FOODSTUFFS.

	MINERAL.	VEGETABLE.	ANIMAL.
Acid or alkali. .	Sod. or pot. carbonate . . Sod. or calc. phosphate (acid)	Tartaric, citric, malic, acetic.	Lactic, oleic, butyric, stearic.
Volatile ..	Water	Essential oils, esters, alcohol, acetic acid.	—
Ash Mineral matter	Sod. pot. chloride ; sod. pot. carbonate.	Salts of tartaric, citric, malic, acetic as carbo- nates	Phosphates . pot. calc., mag., sod. ; Chlorides : pot. calc , mag. sod.
Soluble in petro- leum ether.	—	Coconut, olive, cotton seed, palm, arachis, essential oils (alkaloids)	Stearine, oleo, fish oils, lard (lecithin).
Carbohydrates . Starches ..	—	Wheat, potato, barley, rye, arrowroot, rice, oats.	Lactose
Sugars ..	—	Cane, glucose, maltose ..	
Protein ..	—	Gluten, Globulins ..	Casein, gelatin, peptone, albumen.
Fibre (insol in boiling NaOH)	—	Cellulose.	—

Group 4. Carbohydrates. Positive reaction with Molisch's reagent.

(a) Sugar. Reduction of Fehling's solution.

(b) Starches. Reacting with iodine.

Group 5. Proteins. Positive reaction with Millon's reagent.

Group 6. Fibre. Cellulose.

Group 7. Colouring matter.

Group 8. Preservatives.

Acidity or Alkalinity.

The sample itself or a solution of the sample in distilled water, if it is a paste or solid, is tested with litmus paper and the condition, whether acid or alkaline, is noted.

Fats and Oils—Group 3.

A small portion of the sample is boiled in a test tube with petroleum ether. The ether is then filtered off and evaporated on a perfectly clean watch glass. The presence of any residue after evaporation indicates that a quantitative estimation of this ether extract must be made.

Carbohydrates—Group 4.

Molisch's reaction.

Dissolve a very small quantity of the sample in distilled water in a clean test

tube. Add to this 2 drops of a 20 per cent. solution of alpha-naphthol in alcohol. Mix. Then, very carefully, pour down the side of the tube 2 c.c. of concentrated sulphuric acid.

If carbohydrate is present a deep violet coloration is developed at the junction of the two layers of liquid.

Protein—Group 5.

Cole's modification of Millon's reaction.

Solutions Required for Reagent.

1. 10 per cent. solution of mercuric sulphate in 10 per cent. sulphuric acid.

2. 1 per cent. solution of sodium nitrite. A very small amount of the sample is taken in a perfectly clean test tube.

If the sample is a liquid an equal volume of the mercuric sulphate solution is then added. If it is a solid about 1 c.c. of the mercuric sulphate solution. Should the sample contain a considerable amount of salt (which will have been noticed under "Taste") it will be necessary to add double as much of the mercuric sulphate solution.

The tube and its contents are now boiled for half minute and then cooled under the cold water tap. A yellow precipitate may be formed. Now add to the tube one drop of the sodium nitrite solution and

warm very gently. If protein is present either the solution or the solid in the tube will turn gradually pink or red.

DETAILED QUANTITATIVE ANALYSIS.

Preparation of the Sample.

Care must be taken to ensure that the sample for analysis is homogeneous.

In the case of a solid this may be done either by mincing or milling or crushing in a mortar.

Pastes must be thoroughly stirred each time before weighings are made of the sample to avoid the separation of any heavy material or the "sweating" of moisture.

Liquids must be shaken thoroughly to disperse evenly through the sample any sediment or crystals.

Determine the Acidity or Alkalinity.

The sample or a solution of it has been tested with litmus and found to be either acid or alkaline.

Five gms. of the sample is weighed into a beaker. Recently boiled and cooled distilled water is added and the weighed amount of sample is stirred thoroughly into it.

The solution is titrated with half-normal sodium hydroxide or sulphuric acid using both methyl orange (for carbonic acid) and phenolphthalein (for alkalies or organic acids) as indicators.

On the basis of this result a more careful and accurate titration is made on an appropriate amount of the sample using deci-normal acid or alkali.

Should a solution of the sample be of such a colour that the colour change of the indicator is masked, this can be overcome by "spotting." After each small addition (in the first titration after each addition of 1 c.c.) a spot of the solution is taken out on the end of a glass rod and placed on a white glass tile. A spot of the indicator is then placed next to it and when the two spots coalesce any colour change becomes apparent. In the final titration this should be done after each addition of .1 c.c. once the neutral point is approached.

The sample is tested qualitatively for the particular acid or alkali present. Reference should be made to any characteristic taste or smell noticed previously.

The acidity of fruit preparations is generally given as citric acid.

Potassium carbonate may sometimes be found in "soluble cocoa" preparations.

Acetic Acid in the Presence of Non-volatile Acids.

An estimation of total acidity is made as previously described, a further quantity of 5 gms. is weighed out and evaporated to dryness. 10 c.c. of water is added and the solution is again evaporated. This is repeated three times.

The sample is again diluted and titrated this time with deci-normal sodium hydroxide using phenolphthalein as indicator.

The difference of the two titrations is calculated to acetic acid.

Group 1.—VOLATILE at 100° C.

This will include water, alcohol, acetic acid and essential oils.

An estimation should be made in all cases no matter how apparently dry a sample may seem.

How to Deal with Powders.

5 gm. is weighed into a previously heated and weighed nickel dish which is then heated in a water bath at 100° C. for six hours or till of constant weight. The loss by difference is found and the percentage loss is calculated.

Precaution if Sugar is Present.

In the case of samples containing sugar, particularly in conjunction with acids, decomposition will take place at 100° C. Such samples must be dried at a temperature which does not exceed 70° C. in vacuo.

Dealing with Pastes—

2 gm. of the sample is weighed and dissolved in distilled water and then stirred into a shallow basin containing dried, clean Calais sand (40-60 mesh) which has been previously weighed. The basin and its contents is dried for a minimum of 16 hours in a cellular water bath at 100° C. The loss of weight so found is calculated to percentage loss at 100° C.

—and Liquids.

5 gm. of the sample is dried in a weighed nickel or platinum dish for six hours or till of constant weight. In the case of samples containing considerable amounts of salt, gummy matter or protein such as

albumin the estimation should be made as for pastes.

Estimation of Alcohol in Liquids.

100 c.c. of the sample, which will always be a liquid, is measured into a distillation flask and made slightly alkaline with sodium hydroxide. 50 c.c. of this is distilled and collected and the specific gravity of this amount (at room temperature) is found by hydrometer or gravity bottle. The percentage of alcohol is found from standard alcohol specific gravity tables. This amount is halved so giving the amount of alcohol present in the original sample.

Group 2.—MINERAL MATTER.

2 gm. of the sample is weighed into a counterpoised porcelain or platinum crucible. This is then charred carefully and slowly in a Bunsen burner flame to avoid loss by spluttering. The ashing is completed in a muffle furnace. The crucible is cooled in a desiccator and weighed and the weight of ash so found is calculated to percentage.

Care must be taken not to apply too great a heat as certain salts (e.g. potassium chloride) may be volatilised, giving an erroneous result.

The only necessary estimation to be made on the ash is when salt is there in considerable quantity and has obviously been added. This is done by the Volhard method described earlier in this work.

Group 3.—SOLUBLE IN PETROLEUM ETHER.

The portion of the sample used for the "estimation of moisture" or another portion, weighed and dried, is used.

The dried and weighed amount of the sample is transferred to a double thickness Whatman Soxhlet thimble. Extraction is made into a previously weighed Soxhlet flask using petroleum ether (B.P. 40-60) for a minimum time of three hours.

The ether is distilled off at the end of this time. The flask is disconnected, dried in a vacuum desiccator and weighed. It is then dried in a bath at 100° C. for two hours, desiccated and weighed again.

The difference between the two weights, before drying at 100° C. and after, gives the amount of *essential oil*.

The first weight gives *total soluble in petroleum ether*. This may contain oils and fats, alkaloids and lecithin.

Precaution.

If under "smell and taste" a distinct flavour or smell such as lemon or vanilla has been found, the extraction must be made on a portion of the sample which has not been dried and the subsequent drying of the extractive must be made in a vacuum desiccator.

If the sample is a liquid it should be extracted in a separating funnel by several washings with petroleum ether.

Alkaloids.

The only alkaloids to be found in food-stuffs are caffeine, theine and theobromine. Their presence will have been noticed in the examination under taste by the distinct flavours of tea, coffee or cocoa.

Tests.

The petroleum ether extract is washed several times with distilled water. The water washings are collected and evaporated carefully in the presence of chlorine water (5 c.c.). The residue, if alkaloids are present, will be yellow and further heating turns it a reddish colour. Moistened with ammonia, a purple colour is obtained.

The quantitative estimation of the alkaloid content is unnecessary.

Lecithin.

The water extract from the petroleum ether extraction may also contain lecithin.

Test.

A small amount of this residue is evaporated to dryness, and ignited to an ash. It is digested with strong nitric acid until it is dissolved. The solution is then treated with ammonium molybdate solution for phosphate. A yellow precipitate indicates lecithin and egg-yolk as part of the sample.

The ether extract has been divided into :—

1. Water soluble. Alkaloids and lecithin.
2. Volatile at 100° C. Essential oils.
3. Residue from the above. This consists of fats and oils.

Fats and Oils.

These are evaluated on the basis of

their melting points, iodine values and saponification values. Unless the bulk of the sample is a fat or oil, the determination of these values will be a somewhat difficult matter; but in this case the rest of the analysis should supply sufficient evidence to identify the nature of this residue as it will naturally be linked with the main basis of the food.

Where the nature of the sample is such that a detailed analysis can be made, figures under these headings should be obtained:—

	Melting Point.	Iodine Value.	Saponifica- tion Value.
Beef fat ..	47-50	38-45	193-200
Lard ..	35-46	57-66	193-199
Olive oil ..	—	80-87	190-195
Arachis oil ..	—	87-98	190-196
Cotton Seed ..	—	105-115	192-195
Sesame ..	—	103-110	188-193
Cocoonut oil ..	22-26	7.9-8.8	255-258
Palm kernel ..	25.5-28.5	14-19	245-248

Saponification Value.

The saponification value represents the number of milligrams of potassium hydroxide required completely to saponify 1 gm. of the fat or oil.

Estimation.

Solutions required.

1. Solution of alcoholic potash, approximately half-normal.
2. Solution of hydrochloric acid, accurately half-normal.

The alcoholic potash is made by dissolving 40 gm. of pure potassium hydroxide in a minimum quantity of distilled water and making up to 1,000 c.c. with 95 per cent. alcohol. The solution is allowed to stand overnight and then the almost clear liquid is decanted off.

2 gm. of the filtered fat is weighed into an Erlenmeyer flask. Into this is pipetted 25 c.c. of the alcoholic potash solution. This must be done very accurately and the number of drops which fall after the bulk of the liquid has run from the pipette should be counted.

In the same way another 25 c.c. of this alcoholic potash solution is pipetted into another similar flask. It is essential that these two flasks be of the same quality of glass otherwise there is a possibility of error.

The two flasks are now connected to reflux condensers and boiled. After the fat in the one has gone into solution the

boiling is continued gently for another 30 minutes with frequent shaking.

Both are then disconnected. Ten drops of phenolphthalein, 1 per cent. solution, are added and both are titrated with the half-normal hydrochloric while still hot.

The titration figures for both flasks are taken.

Calculation.

$S =$ gms. of fat or oil.

$A =$ c.c. of half-normal hydrochloric required in the blank or control flask.

$B =$ c.c. of half-normal hydrochloric required in the test proper.

Saponification value:—

$$\frac{(A-B) \times 0.02805 \times 1000}{S}$$

Iodine Value.

The iodine value represents the percentage of iodine absorbed by an oil or fat.

Estimation.

Solutions required.

1. Wij's solution of iodine monochloride.

A 10-gm. tube of iodine trichloride is dissolved in 200 c.c. of glacial acetic acid and 12 gm. of iodine is dissolved in a further 500 c.c. of acetic acid. The solution of iodine is added gradually to the solution of iodine trichloride until, after shaking, the colour of the iodine is no longer absorbed by the iodine trichloride solution. A slight excess of iodine solution is added and then the bulk is made up to 1,000 c.c. with acetic acid and heated for 15 minutes on a boiling water bath.

2. Carbon tetrachloride. (Pure.)
3. Potassium iodide. (10 per cent. solution.)
4. Sodium thiosulphate. Deci-normal.
5. Solution of potassium dichromate. 3.863 gms. in 1,000 c.c. of distilled water.
6. Pure hydrochloric acid.
7. Soluble starch solution (.1 per cent).

Standardisation of the Sodium Thiosulphate Solution.

5 c.c. of hydrochloric acid, 10 c.c. of the potassium iodide solution and 50 c.c. of distilled water are placed in a 200 c.c. flask. 20 c.c. of the potassium dichromate solution is then pipetted very accurately into this and is titrated with the sodium thiosul-

phate solution using the soluble starch as an indicator.

20 c.c. of the potassium dichromate solution will liberate .2 gm. of iodine and from this the value of the thiosulphate solution can be calculated.

A preliminary test is run on the fat or oil so that the quantity of the fat taken for the actual estimation may be adjusted so that not more than half the Wij's solution is used.

The Titration.

Weigh into a clean, dry flask (200 c.c.) approximately the necessary amount of fat. The exact weight taken is noted. Warm slightly and add 10 c.c. of carbon tetrachloride to get the fat or oil into solution. Now add 25 c.c. of the Wij's solution, measured accurately, stopper the flask, shake and set aside in a dark place for one hour.

A blank test is run parallel with this using exactly the same quantities of solution, but of course no fat or oil.

After the hour's standing add to both flasks 10 c.c. of the potassium iodide solution and 50 c.c. of water.

Titrate with the sodium thiosulphate solution until the colour of the solution is faintly yellow. Now add from 5 to 10 c.c. of the starch solution and continue the titration gradually until the blue-violet coloration disappears after shaking. The number of c.c. used for the titration is noted. The blank is titrated in the same manner.

Calculation.

A = Number of c.c. used in blank titration.

B = Number of c.c. used in test titration.

I = Weight of iodine equivalent per c.c. of sodium thiosulphate calculated from the potassium dichromate standardisation.

W = Weight of fat or oil used.

$$\text{Iodine value} = \frac{(A-B) \times I \times 100}{W}$$

Group 4.—CARBOHYDRATES.

If carbohydrates have been found in the preliminary qualitative analysis, test for :—

Starch.

A small quantity of the sample, made neutral, is placed on a white glass plate. A few drops of a dilute iodine solution are

added to it and the sample is broken through it with the aid of a glass rod. Should particles of the sample be stained an intense blue, starch is present.

Estimation.

This is described on page 383.

Identification.

The only method of identifying the particular type of starch used is by comparison by microscope with known specimens. The purpose served by all starches is generally the same, but it is as well to remember that there are some slight differences in taste between the various starches and also some differences in their commercial usage.

Wheat starch is found in cakes, biscuits and bread.

Arrowroot is used for its whiteness, its silky texture and its thickening quality.

Cornflour, or maize starch is found in custard powders, blancmanges and ice-cream.

Pea flour retains its characteristic flavour and its colour.

Carbohydrates—Sugar.

A small amount of the sample is dissolved in distilled water and filtered. The filtrate is tested with Fehling's solution directly and after inversion by boiling with acid and if it gives a positive reaction, i.e. reduces the Fehling's solution, sugars are present.

A further amount of the filtrate is tested with the protein reagent used in the qualitative examination. If protein in a soluble form is present, the modified method of estimation of sugars is used.

Estimation of Sugars in the Absence of Soluble Protein.

5 gm. of the sample is weighed into a small flask. Cold distilled water is added and the flask is vigorously shaken. After settling, the supernatant liquid is decanted off through a filter and the residue in the flask is washed again in the same way twice. At the third washing the whole mass is transferred to the filter where it is washed several times with cold distilled water.

This filtrate is neutralised if necessary and made to a definite bulk with distilled water. It is then estimated with Fehling's solution both before and after inversion.

Estimation of Sugars in the Presence of Soluble Protein. W. B. Smith Method.

Five gm. of the sample is dissolved in 25 c.c. of distilled water. Six gm. of solid picric acid and 60 c.c. of a 20 per cent. solution of phosphotungstic acid is added. The solution is shaken vigorously and made up to 100 c.c. It is shaken again and then filtered.

60 c.c. of the filtrate is collected and 5 c.c. of strong hydrochloric acid is added together with 3 c.c. of water. The solution is immediately filtered and the sugar content is estimated by titration against Fehling's solution.

Estimation of Sugar by Fehling's Method in Both Cases.

Solutions required—

1. Copper solution.

34.639 gm. of pure copper sulphate is dissolved in distilled water and made up to 500 c.c.

2. 178 gm. of pure Rochelle salt.

50 gm. of pure sodium hydroxide is dissolved in distilled water and made up to 500 c.c.

Equal portions of solutions 1 and 2 make up the Fehling's solution used for the estimation.

3. Standard sugar solution.

1.9 gm. of pure cane sugar is dissolved in about 200 c.c. of distilled water. 15 c.c. of normal hydrochloric acid is added and the solution is boiled for two minutes. The solution is then cooled and 15 c.c. of normal sodium hydroxide solution is added and the solution is made up to 1,000 c.c.

Indicators.

A starch solution is made by boiling .1 gm. of Lintner's soluble starch in 100 c.c. of distilled water. To 25 c.c. of this is added 2.5 gms. of potassium iodide. Two drops of this solution and one drop of a 10 per cent. acetic acid solution spotted on a white plate are used to indicate the complete reduction of the copper solution.

Estimation.

10 c.c. of the mixed Fehling's solution is pipetted into a porcelain dish of about 200 c.c. capacity. 40 c.c. of distilled water are added and the solution is boiled for 30 seconds. 5 c.c. of the standard sugar solution is then added and the solution is boiled for a further 30 seconds. This is repeated five times. If the

Fehling's solution is accurate and the above conditions have been strictly observed, it should require exactly 25 c.c. of the standard sugar solution completely to reduce the Fehling's solution.

From this the equivalent of 10 c.c. of Fehling's solution in grams of sugar is found. The usual equivalents are as follows:—

10 c.c. of Fehling's solution are equivalent to

0.0475 gm. of cane sugar (after inversion).

.05 gm. of dextrose or levulose.

.067 gm. of lactose.

.0807 gm. of maltose.

A preliminary titration should be carried out so that the final and accurate determination may be such that approximately the same amount (25 c.c.) will be used in this titration, so keeping the conditions of the estimation comparative.

A direct titration is made and then a further portion of the solution to be tested is inverted. Any difference in the two titrations indicates the presence of cane sugar and should be calculated as such.

The titrations are complete when a drop of the supernatant liquid from the dish, carried out on a glass rod, no longer produces a blue coloration in the indicator.

Cane sugar is the usual sugar used in foodstuffs. Its presence will be obvious from taste and from the necessity to invert before it will reduce Fehling's solution.

Maltose may occur in some cereal foods.

Lactose, or milk sugar, will occur in conjunction with a milk source.

Dextrose will be found in conjunction with a fruit base.

Group 5.—PROTEIN.

The sample gives a positive reaction to Cole's modification of Millon's reaction.

Estimation.

One gm. of the original sample is weighed and transferred to a Kjeldahl flask. 20 c.c. of phospho-sulphuric acid (described page 111) are added, in the presence of a trace of copper oxide. The solution is boiled until of a pale straw colour and all trace of organic matter has been destroyed.

The solution is then diluted with 80 c.c. of distilled water and after cooling is steam distilled having been made alkaline with sodium hydroxide into half normal sulphuric acid (20 c.c.).

The titration figure so obtained is converted to nitrogen and then to the appropriate protein figure by factor.

Protein factors :—

General (includes eggs, meat, legumes)	6 25
Wheat flour	5 70
Milk	6 38
Gelatine	5 55

Identification.

Eggs.—The characteristic protein of eggs is albumin which can be recognised by its coagulation in a water extract on boiling. The presence of lecithin in the ether extract will be confirmatory.

Milk.—Casein. If casein is heated with strong hydrochloric acid a violet coloration is produced.

Meat.—Meat contains a group of proteins, albumose, gelatin and peptone, all of which, with the exception of peptone, are precipitated from a saturated ammonium or zinc sulphate solution. Peptone is precipitated by tannic acid. If meat is suspected, the sample should be tested for creatinine by Jaffe's reaction (page 211) and if present should be estimated by the method there described.

Cereals.—The characteristic protein is gluten. In all cases, except certain sugar and starch-free diabetic diets, the presence of starch in quantity gives sufficient indication that the protein may be classed as gluten.

Gelatine.—In the case of jelly preparations this may be added. Its presence may be found by dissolving in hot water, evaporating almost to dryness and then adding a few drops of formalin solution and baking for at least an hour at 100° C. On adding warm water to this residue it does not go into solution. Tannic acid forms an insoluble gummy precipitate with gelatine.

Group 6.—CELLULOSE.

The cellulose content of a food is generally of little consequence. It occurs only as a part of whatever vegetable

matter may be present, i.e. the cellular part of starch, the husk of whole grains or the husk of spices.

If it is present in quantity the whole of the alkaline solution in the estimation of starch should be filtered through a tared filter paper and washed free of all trace of starch and potassium hydroxide with boiling water. The paper and its contents are then dried and weighed.

Group 7.—COLOURING MATTER.

To comply with the food laws of most countries to-day the addition of any mineral colour is prohibited and the colours used in foodstuffs are mainly water soluble dyes which are used in too small a quantity to make their identification, except by comparison, practical.

Group 8.—PRESERVATIVES.

These are described on page 902.

Results Obtained in an Analysis.

Essentially any analysis will result in figures in some or all of the following groups :—

Volatile.

Water.
Alcohol.
Acetic acid.
Essential oils.

Inorganic.

Mineral matter. Ash.

Organic.

Soluble in ether—

Fats and oils.
Alkaloids.
Lecithin.
Essential oils.

Carbohydrates—

Sugar. Cane.
Reducing.
Starch.

Protein.
Cellulose.

NITRO-CELLULOSE LACQUERS

PART II.—ROUTINE TESTS AND ANALYSES

By W. F. WILSON,

Chief Chemist, Messrs. Cellon, Ltd.

WE have emphasized in the previous article the need for careful routine tests on all raw materials if good quality products are to be produced and manufacturing troubles are to be avoided. The following remarks apply to ingredients for commercial lacquers and not, of course, to those for government specification finishes.

Sampling.

Intelligent sampling is necessary before useful tests can be conducted, and care must be taken to ensure that the samples taken are fairly representative of the batch of raw material. It should be borne in mind that most lacquer ingredients to-day are of a very consistent and high level of quality. The following scheme of sampling is suggested:—

Nitro-cellulose.

Owing to its nature and to the sinkage of the damping agent it is impossible to take a true sample and it is virtually impossible to determine the percentage of damping agent present; therefore the amount quoted by the makers has to be taken on trust. One drum in every four or five may be opened and 1-lb. samples blended.

Resins

May be packed in

bags or cases or, if semi-liquid, in drums. A $\frac{1}{2}$ -lb. sample from one container out of five should be sufficient.

Solvents.

When delivered in bulk, probably only one pint sample per tank is necessary, but in the case of large deliveries two may be taken as the solvent is pumped or run from the tank-car. When the liquids arrive in 50-100 gal. drums, pint samples may be drawn from every fifth drum. All bottles, siphons, taps, etc., should be perfectly clean.

Pigments.

Although the more frequently used colours may arrive in batches of 10 to 20 casks, the heavier or more expensive colours may come in one or two containers at a time. In either case, as with solid resins, care should be taken that samples are not drawn solely from the top layers of the casks, and some form of sampling device may be used for tapping the middle of the cask.

Apparatus for Raw Material Testing.

Beside the usual laboratory apparatus, the following will be necessary: Viscometers, with thermostat, tintometer, micro-

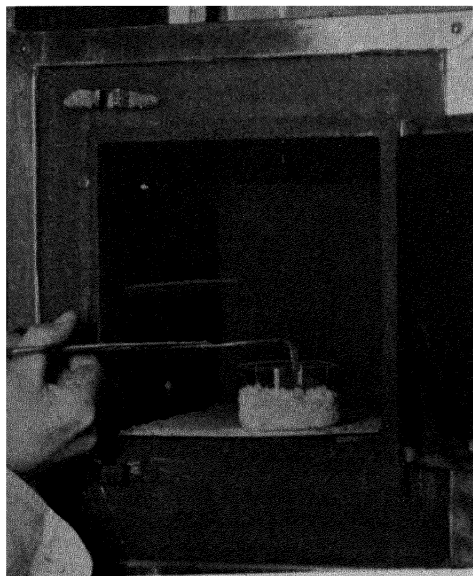


Fig. 1.—DRYING NITRO-CELLULOSE.

The sample is placed in an electric oven kept at 80° C. by thermostat, while the butanol is driven off.

scope, standard distillation apparatus, hydrometers range 0.700-1.300, cryptometer (for hiding power), standard 200 mesh sieve, ultraviolet lamp (preferably of the carbon-arc type) flash-point apparatus, daylight lamp

NITRO-CELLULOSE TESTING.

Only two tests should be necessary for commercial purposes, namely solubility and viscosity.

Solubility.

Having identified the damping agent (usually butanol), dry the sample either in a thermostatic electric oven at 65-85° C or by a current of warm air through a wide vessel or tube containing the cotton. (If an oven is used the interior should be sealed from the element to avoid the risk of igniting the butanol vapour and hence the nitrocellulose.) A 10 or 15 per cent. solution of the dry cotton should then be prepared in a standard cellulose thinner. This solution should be clear and water-white, and should contain no appreciable amount of insoluble fibres (under- or over-nitrated cellulose) or dirt, which, might mar the film or impair its strength. The solution, which is conveniently prepared in a mechanical shaker, should dry in a few minutes to a clear hard film.

Viscosity.

This is a highly important test, and several methods are used, also, besides

the C.G.S. unit, the "poise," various arbitrary units are employed. The Ostwald U-tube viscometer may be used, adapted for lacquers as described in British Standard Specification 2D 50. The solution in a typical thinner described above is suitable. The product of time of flow under gravity through the viscometer, S.G. of the lacquer and factor of the instrument gives the viscosity of glycerin

S.G. 25°/4°
1.2526 having a relative viscosity of 100. The viscometer is kept constant at 25° C in a thermostat, and the lacquer must be free from bubbles

Hercules Falling Sphere Method.

The Hercules falling sphere method used in America uses the following solution —

	Per cent.
Dry nitro-cellulose	12.2
Denatured alcohol	22
Ethyl acetate	17.5
90° benzole	48.3

The solution is placed in a glass tube, and the time taken for a 1-in. steel ball (weight 2.046-2.054 gm) to fall

through 10 in. of the solution is taken as the viscosity of the grade in question, whether $\frac{1}{2}$ sec., 4 sec., etc. One disadvantage of this method is that a very small time has to be measured in the case of low viscosity cottons, and this is surmounted by using more concentrated solutions of these types

Another objection is that the solvents used are liable to vary, not being pure materials.

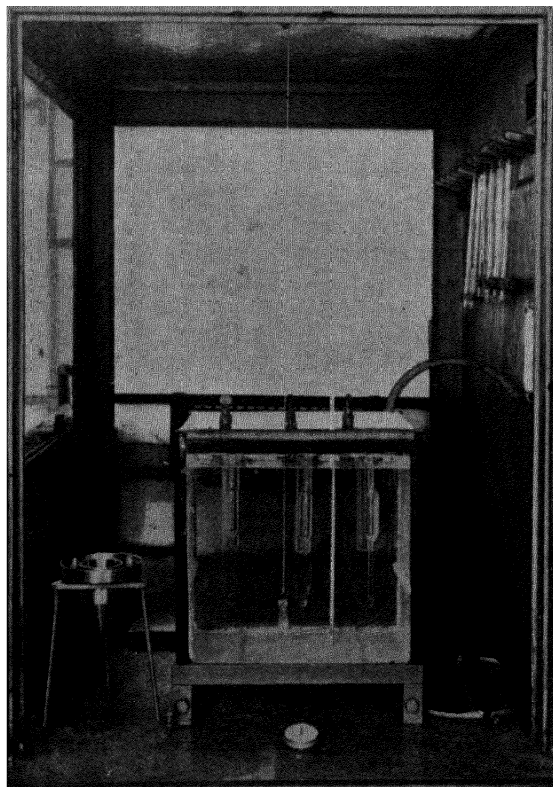


Fig. 2 — CONSTANT TEMPERATURE CABINET FOR VISCOSITY DETERMINATIONS

Three U-tube viscometers are shown in the bath, which is fed by warm and cold water. On the left is a Ford cup efflux instrument

Using a $\frac{1}{16}$ -in. Falling Sphere.

Perhaps the best method is that of Messrs. Nobel Industries Ltd., which employs a $\frac{1}{16}$ -in. falling sphere to give easier timing, and also a purer solvent. According to the grade of nitro-cotton, 10, 20 or 40 gm. of dry sample are dissolved in 100 c.c. of commercially pure acetone diluted to S.G. 0.810 at 15.5° C. with distilled water. At a temperature of 20° C. if the time of fall of the ball be T secs., then the viscosity of the solution in C.G.S. units is very nearly $T/2$.

The U-tube Viscometer.

A method of determining the viscosity in C.G.S. units by the U-tube viscometer is described in the British Standard method for determination of viscosity, No. 188.

A tolerance of about 15 per cent. variation in viscosity is allowable for a given type of nitro-cellulose.

Nitro-cellulose may be tested for water and acidity if desired, but these tests, together with those for stability, etc., are hardly necessary for commercial purposes.

TESTING OF RESINS.

The majority of the resins are, as stated, synthetic, and only minor variations in characteristics are to be expected. The following tests may be made:—

1. Appearance and Odour.

Appearance and odour should match the standard.

2. Colour.

Prepare a 2 per cent. solution and compare colour with that of a freshly made solution of standard sample, or estimate colour quantitatively by tintometer or by titrating dichromate solution in distilled water. This test is of course unimportant for resins used only in dark shades or undercoats.

3. Solubility.

Dissolve 100 gm. in 100 c.c. of a typical thinner and examine the solution for colour, clarity, and residue. Prepare a film on glass, and note drying time and properties of film.

4. Acid Value.

Although the ordinary methods give results difficult to interpret, the value

obtained should at least be consistent from batch to batch, and a determination may be desirable on resins for certain purposes. Weigh out 3 gm. resin and add 100 c.c. alcohol and 100 c.c. benzole. Leave overnight in a corked flask, then titrate with decinormal alcoholic potash. Run a blank on the alcohol-benzole at the same time.

5. Compatibility.

In the case of resins of limited compatibility with nitro-cellulose, such as certain phenolic types, make up a simple lacquer with nitro-cellulose and examine the film on glass under controlled conditions.

6. Softening Point.

Softening point determinations are rarely necessary.

TESTING OF PLASTICISERS.

Owing to their high boiling-points (usually over 300° C.) and the fact that many plasticisers decompose when distilled at ordinary pressure, it is undesirable to attempt a distillation test. For routine purposes, provided that the odour be as faint as is usual and the colour normally pale, only a specific gravity test and an acid value need be taken, the latter being on the lines of the test for resins above. The specific gravities at 15.5° C. for the commoner plasticisers are given below:—

	Specific Gravity.
Diethyl phthalate	1.120 to 1.130
Dibutyl phthalate	1.049 „ 1.056
Diamyl phthalate	1.024 „ 1.027
Castor oil	0.962 „ 0.966
Tricresyl phosphate	1.176 „ 1.182
Barkite (dimethylcyclohexan- yl oxalate)	1.033 „ 1.036
Sipalin M.O.M. (dimethylcyclo- hexan-yl methyl adipate) ..	1.008 „ 1.010
Triacetin	1.160 „ 1.170
Dibutyl tartrate	1.064 „ 1.091

If desired, ester content determinations may be made as described under ethyl and butyl acetates.

The solid plasticisers are of minor importance. If necessary, their quality can be checked by a melting point determination:—

	Melting Point.
Triphenyl phosphate	45° to 48° C.
Ethyl acetanilide ("Mannol") ..	54° C.

TESTING OF SOLVENTS.

Complete details of tests on most lacquer solvents and diluents are given in

the appropriate B.S. Specifications. These apply of course only to the B.S. grades of material, and these grades are preferable for lacquer manufacture. All the tests given in the B.S. Specifications need not be applied in routine testing, but the following points should always be checked:—

Appearance and Odour.

The solvent should be clear and water-white and its characteristic odour not stronger than normal

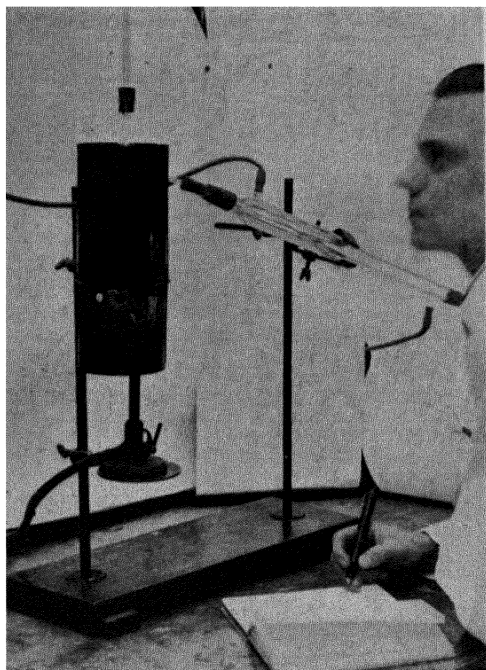


Fig. 3.—THE BRITISH STANDARD DISTILLATION APPARATUS USED FOR TESTING SOLVENTS AND DILUENTS.

Specific Gravity.

This should be determined by hydrometer at 15.5° C. and should not vary more than 0.003 on either side.

Distillation.

100 c.c. of solvent should be distilled in the standard apparatus (B.S. Specification 3D.15). The last 5 c.c. of solvent in the flask may be examined for colour and residual odour, but it is hardly necessary to estimate the non-volatile matter.

Ester Content.

This may be determined on ester

solvents, although actually it is not an infallible index to the solvent power of the liquid, as the presence of a small percentage of the corresponding alcohol is an advantage from the lacquer manufacturers' point of view. $\frac{1}{2}$ -1 gm. of ester is refluxed for 1 hour with an excess, i.e., 25 c.c. of semi-normal caustic potash, and the product titrated with semi-normal hydrochloric acid, a blank is run at the same time.

Water.

All true nitro-cellulose solvents (ketones, esters, ether-alcohols and higher alcohols) should give clear solutions when one part is mixed with nine parts of pure toluole.

Acid Value.

A suitable method for most solvents is to add 25 c.c. to 25 c.c. of neutral alcohol, then titrate with one-hundredth normal caustic potash, using phenol phthalein or methyl red as indicator. The values are usually very low, below 0.01 per cent. as acetic acid.

The specific gravity and boiling range limits for the more important solvents are given below.—

	SG at 15.5° C.	Boiling Range, 95° ₀
Ethyl acetate ..	0.890-0.895	70-80
Isopropyl acetate ..	0.815-0.890	82-95
Butyl acetate ..	0.875-0.890	110-130
Amyl acetate ..	0.870-0.885	118-145
Methyl acetone	0.827-0.833	50-70
Acetone	0.796-0.801	55-60
" Cellosolve " (ethyl glycol)	0.934-0.938	128-137
" Cellosolve " acetate	0.975-0.982	140-160
Butyl " Cellosolve " (butyl glycol)	0.918-0.920	163-174
Cyclohexanone	0.930-0.960	150-165
Cyclohexanol	0.935-0.945	155-170
Ethyl lactate	1.030-1.040	135-160
Butyl lactate	0.987-1.012	185-195
Diacetone alcohol	0.915-0.945	160-166

TESTING OF DILUENTS.

With the exception of the ester content estimation the above tests may generally be used for diluents. As regards industrial methylated spirit both the 64 o.p. and 66 o.p. alcohols are widely used. Various petroleum fractions are also employed as diluents. A suitable type would have a distillation range of 100-130° C. and contain a considerable percentage of aromatic hydrocarbons.

Specific gravities and boiling ranges of diluents :—

	S.G. at 15.5° C.	Boiling Range, 95% ° C.
Toluole	0.868-0.871	109-111
Xylole	0.862-0.865	135-145
66 o.p. industrial spirit (not more than) ..	0.8171	76- 79
Butanol	0.814-0.816	113-119

Dilution Ratios.

These need not usually be determined, but if an occasional check on a petroleum distillate is required, the following method is suggested : Dissolve 20 gm. dry H.X.10 cotton in 100 c.c. butyl acetate. Run in diluent slowly from a burette, stirring constantly and keeping temperature constant, say at 20° C., until definite turbidity

is observed. Then dilution ratio = $\frac{V}{100}$
where V. c.c. = volume of diluent added.

TESTING OF PIGMENTS.

Routine testing of pigments for lacquers involves little change from the ordinary paint methods, bearing in mind that a high standard of quality is set, and that certain special properties must be watched.

Colour and Strength.

By rubbing out in castor oil and adding some clear lacquer the mass-tone of the pigment is observed, also the ease of wetting. The hiding power may be determined by the cryptometer. The undertone and staining power are estimated by reducing 0.1 to 0.5 gm. of pigment with 20 to 100 times its weight of standard zinc oxide and a suitable amount of castor oil. White pigments are tested with standard vegetable black or, better perhaps, with ultramarine blue. The reductions are compared on glass to standard tints, kept in the dark. Prussian blues and toners should be free from "bronzi-ness."

Fineness.

This may be estimated either in oil under the microscope, or by brushing 10 gm. of sample through a 200-mesh sieve with white spirit, when not more than 0.5 per cent. should be retained.

Light Fastness of Doubtful Colours.

This may be checked by exposure tests on a medium tint. These may be made

rapidly under a carbon arc or more reliably in sunlight.

Freedom from Bleeding.

This is important in some cases, and may be tested by warming a little pigment in cellulose thinner and filtering, or by spraying a heavy coat of white cellulose on to a coating of the colour in question. Occasionally even mineral pigments give trouble in this respect because of adulteration or contamination.

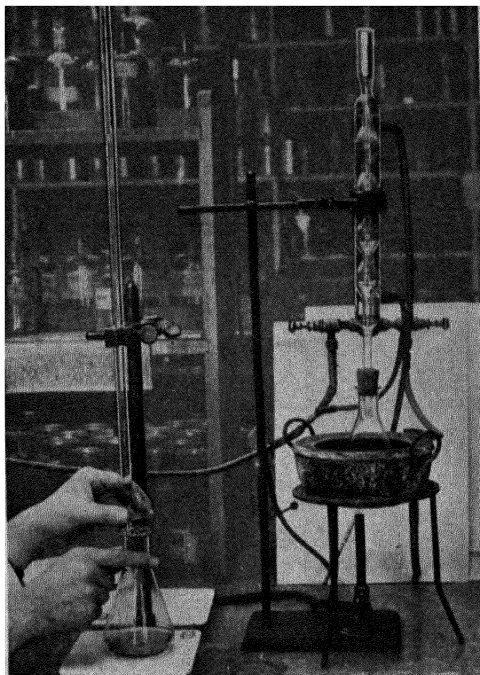


Fig. 4.—ESTER CONTENT DETERMINATION.
The contents of the flask are being back-titrated with acid.

Water-soluble Matter and Moisture.

Chemical tests are generally less important than the physical. Occasionally water-soluble matter or moisture must be estimated ; the former by boiling 5 gm. of colour with 200 c.c. distilled water, followed by filtration, evaporation of an aliquot part of the filtrate and weighing the residue. Moisture is determined by heating 5-10 gm. in a shallow dish in an oven, either at 100° C. for 1 hour or at 85° C. for 2 hours, according to the nature of the pigment. Pigments containing lead should not contain more than 5 per cent.

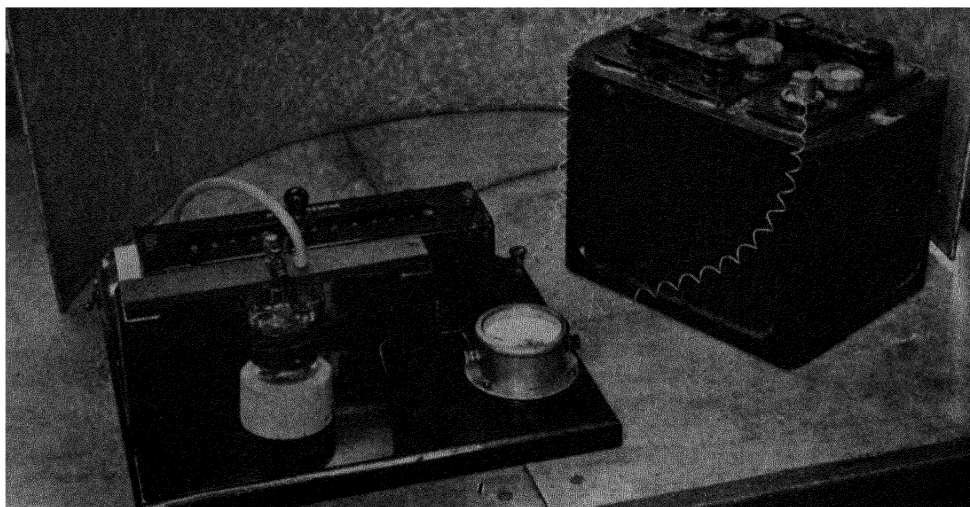


Fig. 5.—APPARATUS USED FOR THE ELECTROLYTIC DETERMINATION OF COPPER IN ALUMINIUM POWDER

The copper is deposited on to a weighed spiral platinum cathode from the acid solution which is kept agitated by a stream of air bubbles.

soluble in cold 0.25 per cent. HCl, calculated as metallic lead on the dry pigment. This of course rules out white lead for cellulose. For specification lacquers various estimations must be made, such as zinc oxide content and lead content in zinc oxide, ferric oxide content in red oxides, etc. These are straightforward analyses and cannot be described here. Generally speaking, for paint and lacquer purposes, chemical analysis of pigments is tedious and of little value.

Ultra-violet Light Tests.

In recent years a good deal of work has been done on the exposure of pigments to ultra-violet light with a view to detecting adulteration exposed by a change in the luminescence. The method has considerable possibilities, but can give very misleading results with an inexperienced worker.

Feeding Up in Cellulose Media.

Pigments which have exhibited a tendency to this trouble should be tested by carefully grinding a small batch under works conditions. If no serious thickening occurs in three days the colour may be considered satisfactory. Some chromes, bronze powders and lakes containing alumina sometimes exhibit forms of this phenomenon.

TESTING FINISHED LACQUERS.

In the modern laboratory rapid but

thorough tests are performed on every batch of lacquer made before it goes into stock, by this means uniformity is assured. The previous tests on the raw material should eliminate any lack of uniformity on that score, but occasionally an error may be made on the works, or inconsistency may creep in, due to some unforeseen circumstance, or to plant inefficiency, such as wear of mills. In these cases the trouble is revealed by laboratory tests, and the material corrected before despatch. No item should be available for use unless definitely approved by one of the chemical staff.

Apparatus Required.

Brushes and spraying equipment, bend and scratch testing machines, frames, fabric and apparatus for airplane dope testing.

The following tests at least should always be made on every batch of lacquer, and the results recorded —

1. Appearance.

Clear lacquers should be examined qualitatively for clarity and colour. No measure of turbidity or tintometer test need usually be taken. Pigmented lacquers in standard or special shades should be checked for shade, applying them as far as possible in the manner in

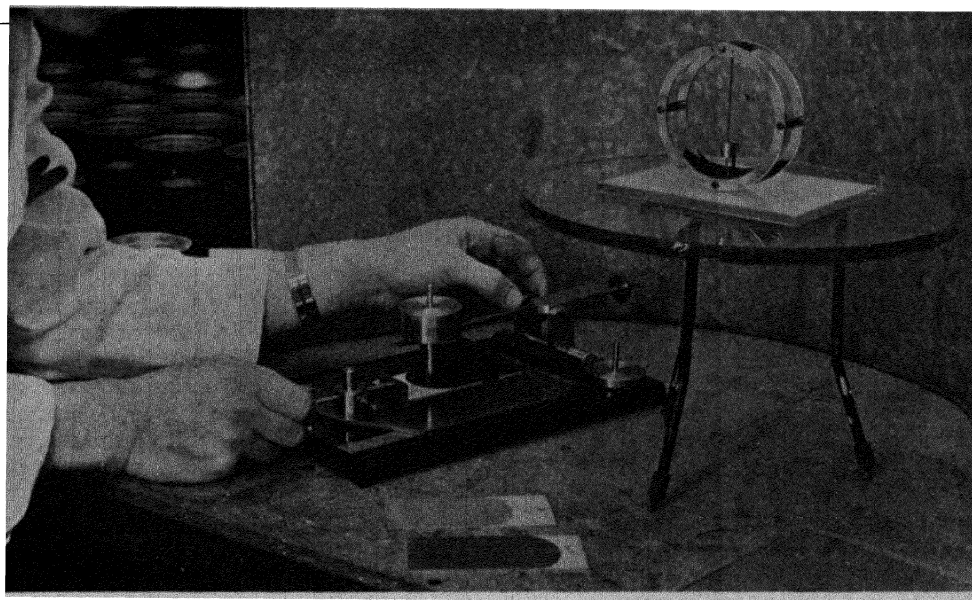


Fig. 6.—TESTING THE HARDNESS OF A FILM.

A lacquered panel is drawn beneath a weighted point. On the right is shown a Sward rocker hardness tester.

which they will be used (e.g., dip, spray, etc.), allowing the films to dry thoroughly and viewing them in diffused daylight. Shade control on the wet lacquer is of doubtful value, and the whole complicated matter of checking colours should be in the hands of experienced men.

2. Viscosity.

The viscosity of all clear lacquers should be determined by the methods previously described, and corrected if necessary. A tolerance of ± 5 per cent. may be allowed. Pigmented finishes, when made from standard base mixtures, need not be tested if no reaction between pigment and medium occurs.

When necessary, the viscosity of pigmented lacquers may be determined with sufficient accuracy in a constant-temperature chamber using a Ford cup viscometer, a very simple efflux instrument.

3. Flow Out on Glass.

By flowing the lacquer on to a glass slide a good idea is obtained of solid content, gloss, covering power, hardness, etc., when the film is compared with standard. If viscosity is correct and the film on glass is satisfactory, no solid content determination need be made. However, as many chemists prefer to check viscosity roughly by a

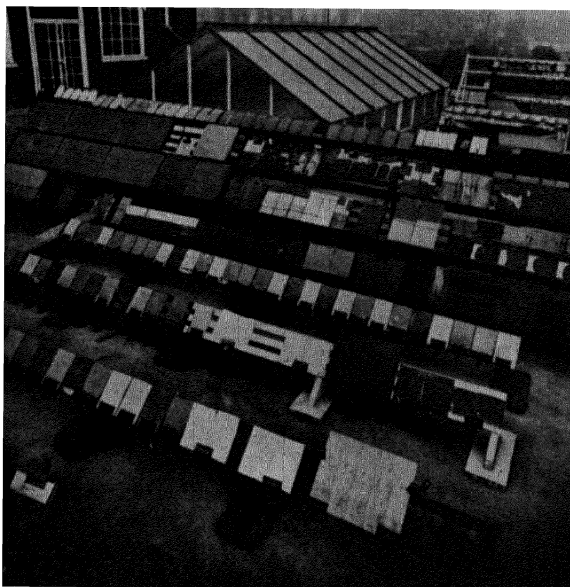


Fig. 7.—A CORNER OF A TEST ROOF WHERE EXPERIMENTAL FINISHES ARE WEATHERED FOR DURABILITY TESTING.

bubble test in test-tubes, and to supplement this by a fairly accurate solid-content test, the latter is described below.—

4. Solid Content.

(a) Pour a weighed amount of lacquer (about 100 c.c.) on a weighed glass plate, to cover about 70 sq. cm. Reweigh the plate after 24 hours at 20° C. (b) As method (a) is generally too slow for works control purposes, it is quicker to use forced-drying. A weighed test-tube is dipped in the lacquer and inverted for an hour to dry, steam being blown into the tube from a steam line or a flask of water. The tube and dry lacquer film are then reweighed, while the amount of lacquer taken is given by the weights of a stoppered wide-mouth bottle before and after dipping.

5. Specific Gravity.

This may be determined as an alternative to solid content.

Tests for Specification or Comparison Purposes.

Many tests may be carried out on the wet lacquer or dry film for specification or comparison purposes. These include the following tests:—

1. Spraying Properties and Covering Power.

A measured amount, correctly thinned, is sprayed on a parti-coloured panel (e.g., black and white check) so as just to obliterate the pattern, and hence the coverage per gallon is calculated. Any tendency to poor flow or "orange-peel" should be observed. By similar spraying

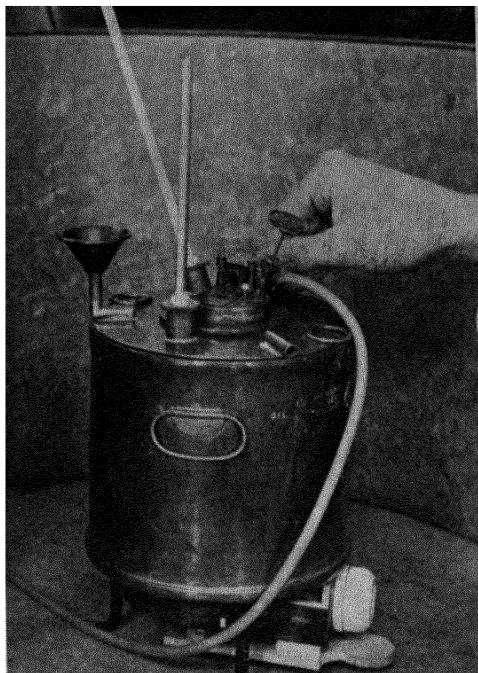


Fig. 8—THE ABEL FLASH-POINT APPARATUS. The cover is open and the vapour has just flashed. Note also draught screen, and the pulley wheel for mechanical stirring of viscous lacquers, etc., for avoiding local heating.

on a sheet of glass and comparison with standard, a direct qualitative comparison of opacity can be observed; while if the test is carried out at say, 75° F. and 80 per cent. humidity, the tendency of the lacquer to "chill" can be noted. The sprayshop should of course be provided with a thermometer and a hygrometer. A chilling test can be run at any desired temperature and humidity by drying a lacquered panel in a closed cabinet provided with heating lamp, water-pan with sliding cover, and circulating fan.

2. Film Properties.

In these tests it is essential that almost all solvent is removed from the film by drying overnight, followed by two hours at 100° C. Adhesion may be tested with the finger-nail using a film prepared in this way on glass. Flexibility is checked by preparing a similar film on a 30 S.W.G. polished aluminium panel, which is then cooled for 1 hour and bent rapidly round a $\frac{1}{8}$ -in. bar. The film should not be cracked or detached by this treatment. Hardness may be estimated in several ways, apart from the time-honoured finger-nail test. One method is to draw at constant speed a coated panel beneath a metal point, radius 0.35 mm., which is loaded by weights. The minimum weight required to scratch through the film is noted. Another way is to prepare a film on glass and observe the number of oscillations given by the Sward rocker hardness tester. Or hardness may be estimated by abrading the film by a constant flow of sand, and noting the time or weight of sand necessary to wear through the film. For these tests it is

essential to use thoroughly dry, uniform films.

To test tensile strength and elongation of lacquer films, as is sometimes necessary in research work, uniform detached films of accurately known thickness must be prepared. Strips of film are then strained in a suitable testing machine and the tensile strength in kilos. per sq. cm. and the percentage elongation are found.

3. Durability Tests.

These fall into two classes, ordinary and accelerated weathering. Space will not permit us to give details, but obviously careful preparation of the test panels is highly important. Normal summer exposure tests with panels facing south and exposed at an angle of 45°, give the best results. An accelerated weathering tester has the panels arranged round inside a slowly rotating drum, fitted to expose the panels in turn to a water spray, radiation from a carbon arc, etc. Such a machine effects a great saving of time and gives valuable results which, however, are often difficult to correlate with those from natural exposure tests.

4. Flash Points.

The ordinary Abel apparatus may be used for determining flash points of cellulose thinners, but for lacquers it is desirable to use a stirring device owing to the poor heat conductivity of the lacquer. Most commercial lacquers flash below 73° F., but the so called high-flash types, usually made on a basis of cellosolve, butanol and xylene, flash above that figure.

5. Airplane Dope Testing.

The testing of finishing materials for aircraft use is highly important.

Airplane dopes must give satisfactory tautening of fabric surfaces, low film weight per unit area, good tensile strength and flexibility and reasonably good durability. To exemplify the tests used, reference can be made to British Standard Specification 2D. 101.

Tautness.

Standard linen airplane fabric is stretched uniformly on a wooden test-frame and the correct number of coats is applied. The tautness is determined by the method given and must be within the given limits.

Elasticity, Brittleness and Adhesion.

Doped fabric is subjected to pressures of 1 and 10 in. of water and the resulting curvatures must be as specified. Also when a bursting pressure is applied the dope film must adhere to the fabric and not crack before the fabric breaks.

Film weight per sq. yd. shall not exceed 3.5 oz. at 25° C. and 95 per cent. humidity.

Further tests are described for inflammability, rate of burning and durability on outside exposure for six months.

ANALYSIS OF LACQUERS.

It is sometimes necessary, as when preparing a lacquer to match a given sample or when investigating doubtful mixtures, to carry out analytical tests. No comprehensive scheme of analysis has yet been devised which is suitable for all types of cellulose lacquers, as such a varied range of products may be present. For commercial purposes it is rarely necessary and practically impossible to determine the exact composition of a sample; usually all that is required is to obtain rapidly a knowledge of the ingredients and their proportions sufficient to prepare a lacquer having similar application and protective characteristics. To gain this knowledge only simple tests and experience are necessary.

We have already described the raw materials which commonly compose the ordinary lacquer, and few others will be encountered. An experienced chemist will obtain a good general knowledge of the sample from these simple tests:—

1. Appearance.

A water-white lacquer will almost certainly be free from resin except possibly a little very pale glyptal or vinyl product.

2. Flow-out on Glass.

Throughout the evaporation period careful note should be taken of the odour of the solvent mixture. All the liquids used have fairly characteristic odours, but the mild odours of alcohol, "cellosolve" and some petroleum fractions may be missed. The drying time, flow-out properties, gloss and hardness should be noticed as they give information on the solvent mixture and proportions of resin and plasticiser. The colour of the film

by reflected and transmitted light should give a good idea of the nature of the pigment, if any, and whether any dye has been used.

3. Heating the Dry Film.

The following substances may be recognised by the odour produced on heating: Castor oil, phenolic resins, drying oils or drying oil-modified resins, camphor (indicating probable use of film scrap), etc.

4. Solid Content and Viscosity.

Both these should be determined by the usual methods.

5. Resin/Nitro-cellulose Ratio.

This may be found fairly accurately thus:—Remove the volatiles by addition of an equal weight of water and distillation at 100° C. on an oil-bath. Dry the solid matter, consisting of pigment (if any), nitro-cellulose, resin and perhaps some plasticiser. 10 gm. of the solids are extracted for several hours in a Soxhlet, using benzole or some solvent which will not dissolve the nitro-cotton. By evaporating the extract to dryness the amount of resin is obtained. In the absence of pigment the nitro-cellulose content may be obtained by difference, and hence the resin/nitro-cellulose ratio. If pigments are present, remove the Soxhlet residue (which now contains no resin) to a flask and extract the nitro-cellulose with acetone. The pigment is removed by centrifuging and the nitro-cellulose extract dried and weighed.

An alternative method is to add to the sample a large volume of benzole to precipitate the nitro-cellulose, which can be filtered off, dried and weighed.

6. Type of Nitro-cellulose Used.

This is judged from the values of the nitro-cellulose content and the viscosity.

7. Type of Resin Used.

It is often difficult to determine exactly the type of resin present and the problem is complicated by retention of plasticiser in the resinous residue. Various chemical and physical tests afford useful indications; among them are:—

(a) Ultra-violet light fluorescence is sometimes characteristic.

(b) Odour on burning.

(c) Melting-point and refractive index.

(d) Solubility tests.

(e) Fastness to light of resin film. Thus a light-fast water-white film would suggest either a very pale alkyd or a vinyl resin, while severe darkening on exposure indicates a phenolic type, etc.

(f) Alkyd or glyptal resins can usually be detected by the formation of fluorescein. A little resin solution is warmed with resorcinol and concentrated sulphuric acid, cooled, and poured into dilute caustic soda.

(g) Various resins give more or less characteristic colours by the Halphen-Hicks or Storch-Morawski tests. In the former test, a drop of resin solution in carbon tetrachloride is placed on a tile, and a drop of bromine solution is applied alongside. The Storch-Morawski colours are produced by dissolving in acetic anhydride, followed by addition of a drop of sulphuric acid.

8. Pigments.

Inorganic colours are usually best examined after ignition of the dried lacquer to remove the film-forming constituents. Owing to the very fine dispersion of the pigments it is very difficult to separate them by settling, filtration or centrifuging. Actually analysis of the pigments is rarely necessary, except in the cases of blacks and whites.

When information has been gained from these tests it should be possible to prepare a lacquer approximating in properties to the sample, and comparative tests will soon show how it should be modified to give an exact match.

9. Identification of the Solvent Mixture.

In practice this is done entirely by odour and trial and error. Exact analysis is unnecessary and very difficult, but details of procedure may be found in Gardner's "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours," Zimmer's "Nitro-cellulose Ester Lacquers," and other books.

BLEACHING OF TEXTILE FIBRES AND FABRICS

By L. G. LAWRIE, A.I.C.

ALL natural textile fibres contain a certain amount of pigment materials in their composition which must be destroyed or removed at some stage during the processing of the fibres before a white material can be obtained. With fibres which occur naturally in a very pure state the amount of colouring matter is very small but is usually sufficient to give the finished fabric a grey or brown appearance if not removed, which detracts from the beauty of the material and often interferes with the production of pure bright colours when subsequently dyed or printed. On the other hand such fibres as, for example, tussur silk or jute contain a very considerable amount of colouring matter and the natural fibres are consequently of a dark shade. The composition of these natural pigments varies considerably from one fibre to another, and even different varieties of the same fibre often contain different natural pigments associated with them.

With most textiles it is necessary to remove or bleach the natural colour in order to produce as white a material as possible, either for sale in this state or because a white fabric is more readily and satis-

factorily dyed or printed. Most of the natural pigments associated with textiles are very resistant to chemical treatment, although with such fibres as cotton and the majority of wool fibres it is comparatively easy to destroy the colour, but on the contrary, other fibres such as tussur silk and camel hair wool cannot be satisfactorily bleached and are therefore often sold in their natural light brown colour.

Bleaching Processes.

The process of bleaching the different

textiles varies considerably according to their nature and in most instances is effected by means of an oxidising agent, but sometimes by means of a reducing agent. The majority of fibres are bleached with one of two oxidising agents. Vegetable fibres are generally bleached by means of nascent oxygen obtained from hypochlorites, whilst animal fibres are either bleached with peroxides or by means of sulphurous acid, in this case a reducing agent. Bleaching methods based upon the use of oxidising agents have been found to be as a rule vastly superior to those based upon the use of reducing

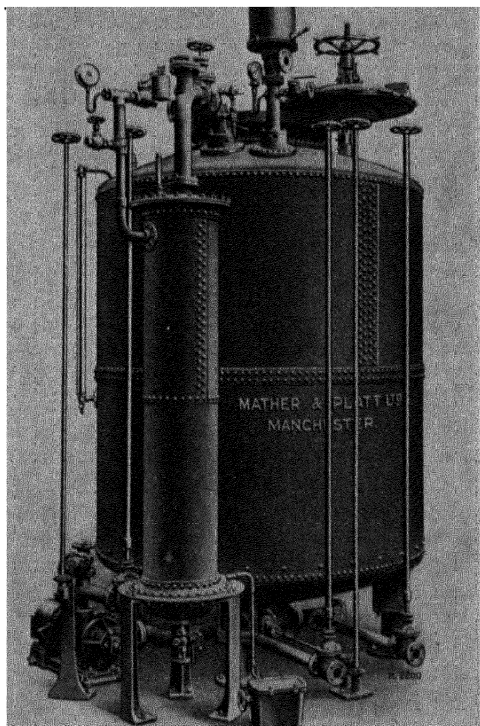


Fig. 1.—A VERTICAL HIGH-PRESSURE KIER IN WHICH THE MATERIAL IS BOILED WITH ALKALI.

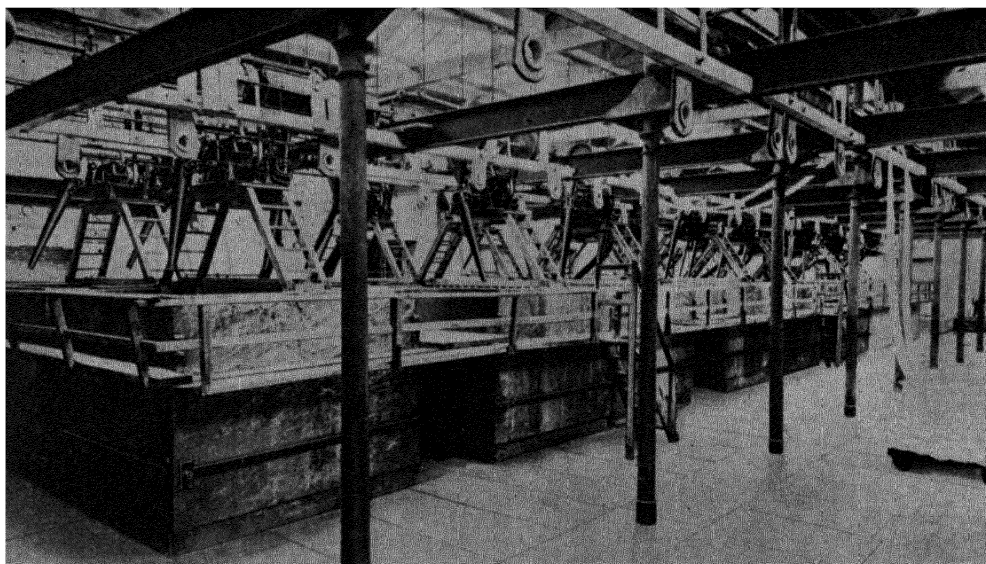


Fig. 2. THE INTERIOR OF A MODERN BLEACH HOUSE

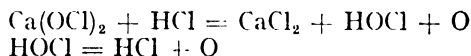
agents. In the first place they are generally more active, and, secondly, the results are more permanent, the colourless products obtained by reduction often returning again owing to oxidation effects produced by exposure to light and air.

Chemicals Used.

The bleaching of vegetable fibres is generally effected by means of either calcium hypochlorite (bleaching powder) $\text{Ca}(\text{OCl})_2$, or by means of sodium hypochlorite NaOCl .

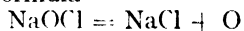
Calcium Hypochlorite $\text{Ca}(\text{OCl})_2$.

Calcium hypochlorite or bleaching powder is obtained by the action of chlorine gas on lime. The commercial product is a soft white powder which although soluble in water always leaves some insoluble residue. On exposure to the air, or, more rapidly, on the addition of a small quantity of acid, it decomposes with the formation of hypochlorous acid, which itself is unstable and evolves oxygen in the nascent state—which oxygen is responsible for the strong bleaching action of the compound. Owing to its very energetic oxidising action it is liable to give rise to the formation of oxycellulose during the bleaching of cotton or linen unless considerable care is taken. The chemical reactions which take place are as follows:—

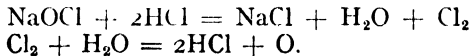


Sodium Hypochlorite (NaOCl).

Sodium hypochlorite can be prepared by the action of sodium carbonate on calcium hypochlorite, by saturating caustic soda with chlorine, or, more usually, by the electrolysis of a solution of common salt brine. The commercial product is sold as a clear liquid of a specific gravity of 28° Tw., which is very considerably diluted for use in bleaching. The bleaching action is effected as with bleaching powder by nascent oxygen, which is evolved on the addition of traces of acid according to the following formula —



but with more acid



Wool and other animal fibres are often bleached with peroxides, either hydrogen peroxide or sodium peroxide, although these bleaching agents are also occasionally used in the bleaching of cotton in place of bleaching powder.

Hydrogen Peroxide (H_2O_2).

Hydrogen peroxide is prepared by dissolving barium peroxide (BaO_2) in acidified water. This can be obtained as a colourless liquid of either 12 vol. (= 3 per cent.) or as 20 vol. (= 5 per cent.)

strength, containing a small quantity of acid, usually phosphoric acid, added as a stabilising agent. A solution of hydrogen peroxide decomposes slowly when cold, but readily when made alkaline and warmed, with the evolution of nascent oxygen.

Hydrogen peroxide is a powerful bleaching agent which has little harmful effect on either animal or vegetable fibres, consequently it can be used for the bleaching of all classes of materials.

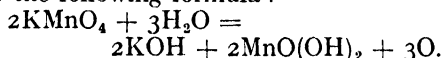
Sodium Peroxide (Na_2O_2).

Sodium peroxide is on the market in the form of a white powder which dissolves in water, with the evolution of oxygen. If dissolved in dilute acid, hydrogen peroxide is formed. Sodium peroxide is used in bleaching in the same manner as is hydrogen peroxide.

Potassium Permanganate KMnO_4 .

Potassium permanganate is occasionally used in bleaching, being a powerful oxidising agent which is capable of destroying many natural colouring matters. It is used in a slightly acid solution, and the material on removal from the solution is stained dark brown owing to the deposition of manganese dioxide on the fibres. This stain can then be removed by treating the material in a weak solution of sodium bisulphite.

The bleaching action which takes place is due to the evolution of oxygen according to the following formula:—



Sulphurous Acid H_2SO_3 .

Sulphurous acid is used to a considerable extent in the bleaching of wool, either in the gaseous form produced by burning sulphur to sulphur dioxide, which combines with the moisture in the wool to form sulphurous acid, or by means of a solution of sodium bisulphite (NaHSO_3).

Sulphurous acid is a powerful reducing agent. It is very probable, however, that it combines with many colouring matters to form a bisulphite compound which is colourless.

BLEACHING COTTON.

Raw cotton usually contains, in addition to colouring matter, a certain amount of fatty and waxy bodies which must also be

removed before a pure white can be obtained. As a rule, the bleaching of cotton is carried out in two stages; the material being subjected in the first place to an alkaline boil, which removes most of the fats and waxes, together with a certain amount of the colouring substances, followed by a bleaching operation proper with hypochlorite, which produces a white fibre. The success of the bleaching operation depends, however, entirely upon the thoroughness with which the preliminary boil has been effected. It is, however, possible to effect a combined boil and bleach by the use of hydrogen peroxide in conjunction with alkali.

The Preliminary Boil.

Although cotton can be bleached in all states of manufacture, it is usually bleached either in the form of yarn or more usually as piece or woven material. The yarn or piece goods are subjected first of all to a prolonged and severe boil or series of boils with caustic alkalies. The nature and severity of this preliminary boil will vary according to the use to which the material is to be put. The most exacting requirements are met with in the "madder" bleach when the cloth is being prepared for dyeing turkey-red, where it is essential that the cloth is freed from all impurities, or thoroughly "bottomed," as it is called. This is also true of cloth destined for calico printing or for the white trade. The success or otherwise of the subsequent bleaching is, as already pointed out, entirely dependent upon the thoroughness with which the cloth has been boiled, and any irregularity of action occurring during the boil is invariably seen in the subsequent bleaching and is then difficult or impossible to correct.

Kier Boiling.

The kier boiling of cotton is carried out in cylindrical iron or steel vessels, known as kiers, in which the cotton is packed, usually about five tons at a time, and into which the caustic liquor is run. The kiers are then closed and heated by steam to a pressure of about 20 lb. for anything from six to twelve hours. The most thorough cleansing is obtained by a boiling treatment with lime, which forms the calcium salts of the fats and waxes present. The cotton is then "soured" with dilute acid, which reacts with the calcium, liberating

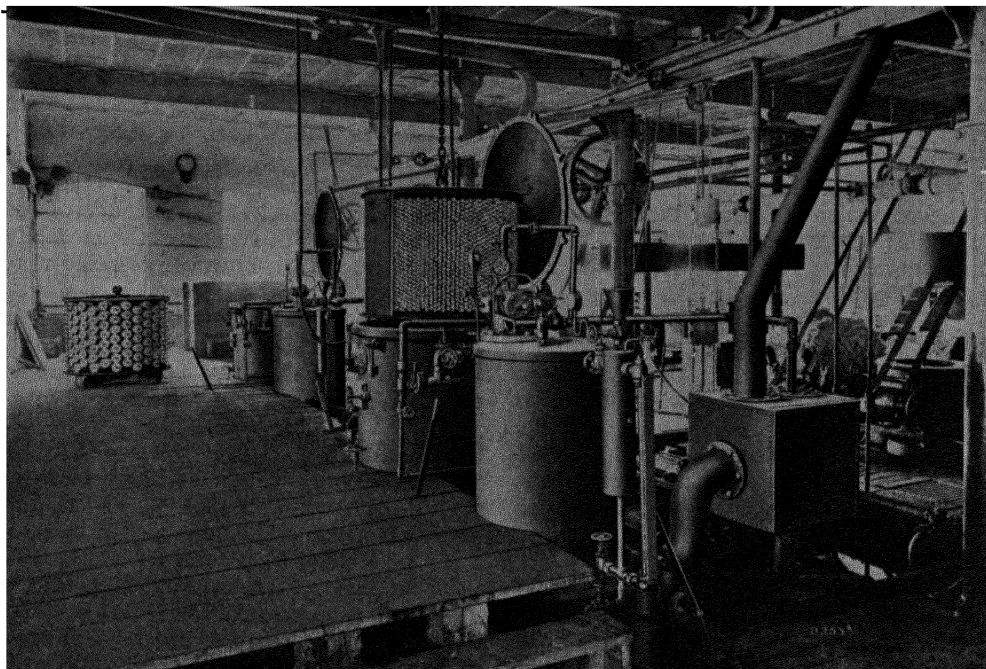


Fig 3.—COP AND CHEESE BLEACHING PLANT.

free fatty acids on the fibre. The cotton is finally given a second kier boil with sodium carbonate when it is ready for the "chemicking," or treatment with sodium hypochlorite.

Caustic Soda Treatment.

The above method is gradually being replaced by a treatment with caustic soda alone, using about a $\frac{1}{2}$ —2 per cent solution of caustic soda at 20 lb. pressure for 12 hours. According to recent researches, the colour of the material boiled in this way can be considerably improved by the addition of a small quantity of a sulphated fatty alcohol such as cetyl sodium sulphate to the alkali liquor.

A milder boil can be carried out by using sodium carbonate instead of caustic soda. Usually a $\frac{1}{2}$ per cent. solution is sufficient for this type of boil, which is usually carried out without pressure, or in a so-called "open" kier.

Bleaching of Colouring Matter not Removed by Alkaline Boil.

After the thorough removal of the fats and waxes, etc., the cotton, consisting of almost pure cellulose, is stained by the kier liquors and also contains a certain amount of natural colouring matter not

removed by the alkaline boil. This colouring matter is then bleached by means of bleaching powder (calcium hypochlorite), or occasionally by means of hydrogen peroxide, the latter being a method which has recently found considerable favour in America and is being adopted to a certain extent in this country.

The bleaching operation with hypochlorite can be effected by circulating a solution of the bleaching powder through the goods, or alternatively by saturating the material with a solution of the bleaching powder and allowing it to lie piled exposed to the air.

Solution of Bleaching Powder—"Chemicking."

The solution of bleaching powder used is very dilute and is made slightly alkaline. It should contain from 2—7 gm per litre of active chlorine, such a solution being made up to a specific gravity of from $\frac{1}{2}$ —2° Tw. Treatment in this solution is called "chemicking."

After chemicking, the goods are well rinsed and then soured with dilute sulphuric or hydrochloric acid to remove residual chlorine, being finally washed again with cold water.

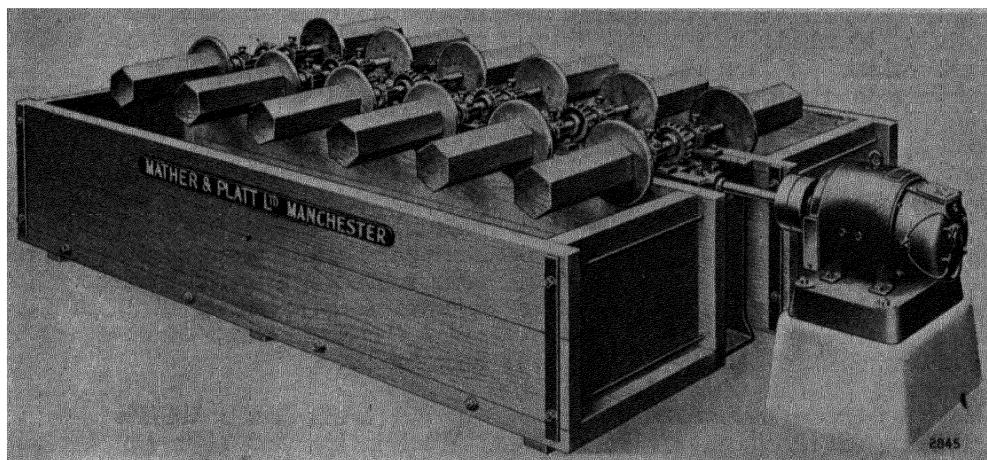


Fig. 4.—HANK WASHING AND RINSING MACHINE.

The mechanism of the bleaching process with hypochlorites has never been satisfactorily explained, but recently a considerable amount of research work has been carried out on the influence of hydrogen ion concentration. In practice, however, the bleaching solution is made definitely alkaline to guard against the formation of oxycellulose.

“Mohr Process.”

In the Mohr or cold bleaching process, no hot kier boiling operation is carried out. The cotton is treated in a kier with a cold solution of bleaching liquor, under pressure, followed by a cold water rinse, a treatment with dilute acid and another rinse. Hydrogen peroxide is then introduced into the kier and the material treated under pressure with this reagent, followed by washing, soaping, a second washing, and finally drying. This process is stated to give an excellent bleached white which is less liable to yellow than the white produced with bleaching powder.

Peroxide Bleaching.

Another method of bleaching cotton which is becoming of increasing importance is one in which the alkali boil and the bleach are carried out in one operation, using hydrogen peroxide as the bleaching agent.

The cotton is packed into an ordinary kier which, however, has been lined with a mixture of Portland cement and lime. The material is treated at a temperature of 185° F. with a mixture of caustic soda,

sodium silicate, hydrogen peroxide and turkey-red oil. All the operations of kier boiling and bleaching are thus carried out in the same vessel without handling, resulting in a considerable economy of time and labour.

An alternative method of peroxide bleaching is to subject the cotton goods to a one-hour boil with a $\frac{1}{2}$ -2 per cent. solution of caustic soda in the usual manner and after the liquor has been run off to wash the goods and run into the kier a solution of hydrogen peroxide and treat the material in this manner for 1½ hours at a temperature of 180-195° F.

The amount of hydrogen peroxide used in this process is about 2 per cent. of H_2O_2 (40 vol.) or 3 per cent. H_2O_2 (30 vol.) on the weight of material to which is added 4 per cent. waterglass 38° Be. as a stabilising agent.

BLEACHING LINEN.

The bleaching of linen is in general outline similar to that for cotton bleaching and consists of a kier boil with alkali, followed by a treatment with hypochlorite. There are differences, however, in the constitution of the two fibres which calls for different treatment in bleaching. In the first place, linen is more sensitive to the action of alkalis than is cotton, and secondly, it contains a much larger amount of impurities which must be removed before a pure white fibre is obtained. In the linen industry a considerable amount of importance is attached to the actual brilliance of the white

produced, which whites are graded as partially bleached, half-white, three-quarter-white, or full-white bleached according to the extent to which the operation is carried out. Linen is bleached either in the form of hanks or in the form of piece goods, the sequence of operations being as follows:—

The First Treatment.

The material is first of all treated as with cotton by boiling in a kier with either 1-2 per cent. caustic soda or 3-5 per cent. sodium carbonate, calculated on the weight of material, together with some soap for about 2-3 hours. After boiling, the material is well rinsed, and treated in the bleaching solution, which is made up of a dilute solution of bleaching powder of from $\frac{1}{2}$ -1 $\frac{1}{2}$ ° Tw. The material is then left in this bleaching solution for from $\frac{1}{4}$ -1 hour according to the amount of bleaching required and is then washed thoroughly. It is finally "soured" in a bath of 1° Tw. sulphuric acid for 15 minutes, rinsed, and the acid neutralised by treatment in a warm (110° F.) solution of 5 per cent. soda ash, being finally washed again.

"Grassing."

The above sequence of operations may be repeated two or even three times in order to obtain the necessary degree of whiteness. Those materials which are required to be fully bleached are then "grassed." This grassing process is an old-established method of bleaching which is still practised in Ireland and other countries where linen is manufactured. The pieces are laid out in the fields and kept damp, being exposed for days or even weeks to the action of sunlight and weather, which eventually bleaches the most resistant colouring matters present in the linen in a manner impossible with chemical treatments.

A More Severe Method.

The following is an alternative and rather more severe method of bleaching linen piece goods. The material is first of all run through a solution of lime water, packed into a kier and boiled for from 8 to 12 hours. After boiling, the material is washed thoroughly and soured in dilute hydrochloric acid of 1 $\frac{1}{2}$ -2° Tw. and again washed. The linen is next subjected to a series of boils, varying in number according

to the amount of bleaching required, in a mixture of caustic soda and sodium carbonate of from 4-6° Tw.

Following these alkali boils the goods are treated alternately with sodium hypochlorite and weak soda, being grassed between each treatment. The cloth is then chemicked in weak hypochlorite of soda solution, soured, and finally washed. During the boiling processes the goods are often rubbed in a special machine which removes small particles of black fibre called "splits" which often appear in linen goods.

BLEACHING WOOL.

Wool is bleached after scouring and spinning in the form of hanks, or, when woven and scoured, in the form of piece goods. There are two main methods of bleaching wool, the oldest but one still very commonly practised being by the use of gaseous sulphur dioxide, the so-called sulphur stoving, and the more recently used method of bleaching with peroxides.

Sulphur Stoving.

The method of bleaching with sulphur is very simple, cheap, and gives a particularly brilliant white to the wool. It is used to a considerable extent for blankets and flannels. It suffers from the disadvantages that the white produced is not permanent—a certain amount of natural colouring matter of the wool returning after a time, especially when the material has been washed—and in addition, goods sulphur stoved generally possess a slight unpleasant smell which is particularly noticeable in damp weather.

The method of carrying out the bleaching operation is very simple. The material to be bleached is moistened or more generally brought straight from the scouring machine in a damp state containing soap and water and is hung on wooden rods in a brick chamber, which can be hermetically sealed. In the chamber is lighted a quantity of lump sulphur, the amount depending upon the capacity of the stove and the quantity of material. The sulphur, which is then left to burn itself out, burns with the formation of SO₂, and this reacts with the water in the goods to give sulphurous acid H₂SO₃, which exercises a powerful bleaching action on the colouring matter in the wool. The

goods are generally left in the stove for 12 hours or overnight and then removed and hung in the air.

Peroxide Bleaching.

The bleaching of wool with hydrogen or sodium peroxide is a more costly operation than is sulphur stoving and is therefore generally reserved for the better qualities of woollen materials. It possesses certain definite advantages over the stoving process in that the white so produced is permanent, the natural colouring matter of the wool not returning on exposure to air or on washing; secondly, the wool possesses no disagreeable odour after bleaching; and thirdly, peroxide bleached wool has less action on dyed materials with which it may be woven than has stoved wool.

The following is a typical method of carrying out a bleach with hydrogen peroxide:—

The plant used is a rectangular bleaching tank which can be made of wood, glazed brick, cast-iron or steel with porcelain or enamel glaze. It is heated with a lead steam coil. The wool, which must first have been scoured, is packed into the tank, which contains 2-4 gall. of 100 vol. (= 30 per cent.) hydrogen peroxide per 100 gall. of liquor. To this solution silicate of soda is added until the liquor reacts neutral to phenol red. The bleaching liquor is heated to a temperature of 120° F. and the wool allowed to remain in the bath overnight, when it is finally rinsed and "blued" if necessary. The bleaching bath may be used for several weeks, further additions of hydrogen peroxide and silicate of soda being added when necessary.

Sodium Bisulphite Bleaching.

Recently the Woollen Research Associa-

tion has worked out a process of bleaching wool based on the use of sodium bisulphite which is stated to be free from the usual impermanency of the usual bisulphite bleaching process and to be unaffected by washing. This process depends upon a strict control of the proportions of SO_2 and caustic soda present in the bath, the active range being 1 part of SO_2 to 1.25 parts of caustic soda. This produces the optimum conditions for the reaction of the bisulphite with the colouring matter, with, it is believed, the formation of a bisulphite compound of the colouring matter in the wool.

BLEACHING SILK.

The natural silk fibre is surrounded by a layer of sericine, which must be removed before the bleaching operation is commenced by a process known as "boiling off" or "degumming." Silk is usually degummed in the form of hanks, and the boiling off process is variously carried out according to whether one is required to remove all or only

part of the silk gum or sericine. The process is the same in both cases and consists of treating the silk in a boiling soap bath, but varies in severity.

Tussur Silk.

Tussur silk is sometimes washed in a dilute solution of hydrochloric acid before degumming in order to remove any lime which may be present and which would otherwise form an objectionable scum of lime soaps during the boiling process.

In degumming, the first operation consists in treating the silk at a temperature just under the boil for 1-2 hours with a solution of Marseilles soap containing 20-30 per cent. on the weight of the silk. During this treatment the silk swells

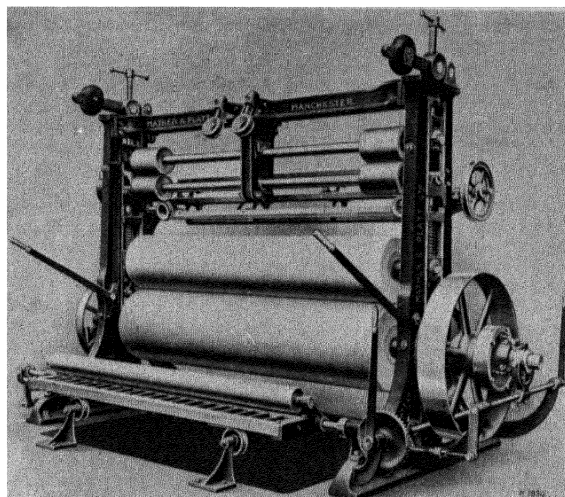


Fig. 5.—SLACK WASHING MACHINE.

considerably and becomes soft and more lustrous. The silk hanks are then treated in a second or third bath made up in the same manner, being finally rinsed in a weak solution of soda ash. To remove the last traces of gum the hanks are finally boiled in a fresh bath containing from 10-15 per cent. soap, rinsed, wrung and dried.

Souple Silk.

Souple silk, which is less thoroughly degummed, is treated for 1-1½ hours at a temperature of 95° F. in a bath containing 10 per cent. soap; immersed for ¼ hour in a solution of aqua regia of 3-4° Tw., rinsed and stoved for from 5-6 hours in a sulphur stove. The sulphur stoving is repeated as often as necessary until the silk attains the desired whiteness.

Ecru Silk.

Ecru silk is degummed to a still less extent, and is only subjected to a treatment in a very weak solution of soap and is then bleached in the sulphur stove.

After degumming, silk is bleached when it is required in the white state or when it is to be dyed in pale shades. The bleaching processes are similar to those used for bleaching wool, the silk being usually bleached with hydrogen peroxide or in the sulphur stove.

Stoving Silk.

Bleaching silk in the sulphur stove is of lesser importance with silk than with wool, but this method of bleaching is still carried out to some considerable extent. It possesses the same disadvantage as is associated with wool in that the natural colouring matters are only reduced and tend to reoxidise back again on exposure to air, or especially on washing in alkaline soap solutions.

Before being stoved the silk is thoroughly wet out in a dilute solution of soap, the damp material then being hung on racks in the sulphur stove. Pans of sulphur are then lit in the stove and the silk allowed to remain for 8 hours or overnight.

Bleaching with Hydrogen Peroxide.

The bleaching of silk with hydrogen peroxide is carried out usually in either a wooden or earthenware tank containing

an enclosed steam coil for heating. The hydrogen peroxide bath is made up with 2½ pints of 100 vol. H_2O_2 for every 12 gall. water, to which is added sufficient sodium silicate to render the bath faintly alkaline. Alternatively one may use a bath made up with 12 vol. hydrogen peroxide, taking an equal weight to that of the dry weight of the goods to be bleached, the bath being made alkaline with either sodium silicate or ammonia.

With either of the above methods the silk is entered well wet out and the temperature raised to 130° F., the silk being treated at this temperature for from 3-4 hours. The temperature of the bath is then raised to 140° F. and the silk treated at this temperature for a further period of 4 hours, when it is finally rinsed and soaped.

Bleaching with Sodium Peroxide.

When making up a bleaching bath with sodium peroxide it is usual to take about 4 lb. of sodium peroxide and 5½ lb. of sulphuric acid to 120 gall. of water. The sodium peroxide is added a little at a time, with constant stirring. Before entering the silk it should be wet out, a suitable bath for this purpose being made up with 1 per cent. Marseilles soap and 2 per cent. soda. The treatment of the silk in the bleaching bath is carried out as given above for hydrogen peroxide bleaching.

Bleaching Silk Hosiery.

After degumming, the hose is packed into net bags and immersed in a bath containing 1 vol. hydrogen peroxide, together with sufficient silicate of soda to render the bath slightly alkaline. The hosiery is treated for about 2 hours at a temperature of 160° F. to commence with, rising to 195° F. at the end of the operation.

Bleaching Silk Crepe.

Silk crepes are bleached in a winch machine containing a 1½ vol. solution of hydrogen peroxide with sufficient sodium silicate added to render the solution faintly alkaline. Bleaching is carried out for 2 hours at a temperature of 160° F., the material being finally washed and dried. The bleaching of Jute and Hemp is dealt with on page 1396.

AUTOCLAVES

NOTES ON THEIR CARE AND MAINTENANCE

By CHARLES H. BUTCHER

THERE are many chemical reactions which proceed much better if they are carried out in a sealed vessel where internal pressure, higher than that of the atmosphere, is developed by the application of heat. Such vessels are known as autoclaves. They are commonly used in the manufacture of dye intermediates, where pressure may be an indispensable factor for the reaction, or where increased pressure gives yields which are far greater than those obtained by other methods of working.

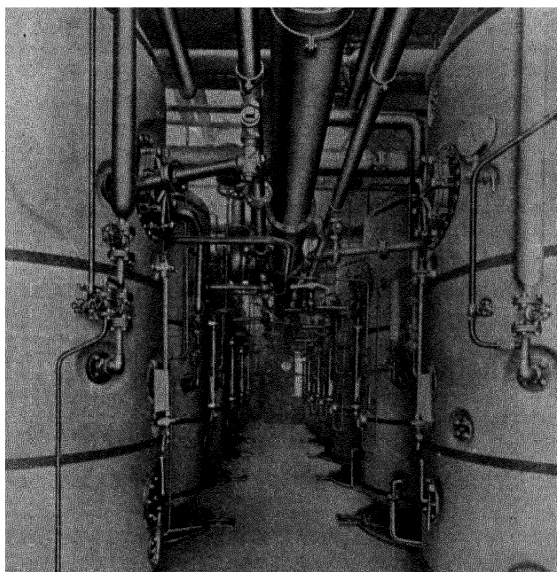
These autoclaves may be provided with steam jackets for use at relatively low temperatures, or oil jacketed for use at much higher temperatures. In addition, there are autoclaves which are directly heated by gas and have no jacket. The material of construction is either tough mild steel, cast steel, or cast iron, an internal lining of vitreous enamel or chemically pure lead often being provided for the purpose of resisting the corrosive action of the chemicals, which is more pronounced at high pressures and high temperatures.

Jacketed autoclaves are more widely adopted than the unjacketed type, because the products which are manufactured by indirect heating

are usually purer and cleaner than are those obtained by the direct heating of an unjacketed autoclave; a slightly higher yield is also obtainable. In some cases the capacity of the vessel may be 300 gallons or more, but for small-scale manufacturing and experimental work the capacity may be only one gallon or even less.

Constructional Details.

In the majority of cases the body of the vessel is made in one piece and is cylindrical in shape with a hemispherical bottom, where a blowing orifice is provided for removing the products of the reaction. To this body a domed lid is bolted, the lid being provided with a charging hole (except in the case of small experimental autoclaves), and a gland and gland cavity for the rotating vertical shaft of the stirrer, which is an essential feature of all autoclaves. The lid also carries a pressure-gauge connection, thermometer pocket, safety valve and blow-off or pressure-release valve for gaseous products of the reaction, and also a bracket to support the bevel wheels by which power is transmitted to the stirrer by belt from main line shaft.



W. J. Fraser & Co., Ltd.

Fig. 1.—PART OF A BATTERY OF THIRTY AUTOCLAVES HANDLING FOOD PRODUCTS.

The Stirrer.

The stirrer is usually of a shape which conforms to the contour of the walls of the vessel, especially in respect of the hemispherical bottom, for it is necessary to keep the charge continuously in motion during the heating operation, in order to prevent overheating and also "settling out." The efficiency of the stirring throughout the operation, with absolutely continuous subdivision of the charge, are the keynotes to success in this particular type of manufacturing process.

Depth and Diameter.

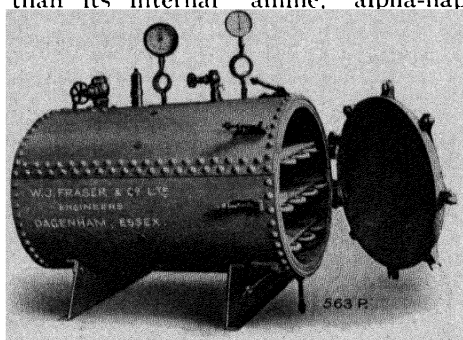
The internal depth of the vessel is usually slightly more than its internal diameter, because these proportions are ideal for heating purposes, and also because the use of an autoclave which is deeper will create difficulties with regard to keeping the contents properly subdivided and intermixed, especially where the component parts of the charge have a tendency to separate out in two layers—the manufacture of beta-naphthylamine from beta-naphthol being a typical autoclave reaction of this nature. In other cases where the contents of the autoclave are mixable and remain fluid throughout the process—as in the preparation of alpha-naphthylamine sulphonic acids from the corresponding naphthol sulphonic acids—the autoclave may be somewhat deeper if necessary to obtain the desired capacity, as it is not advantageous to increase the internal diameter beyond 3 ft. 6 in. on account of the stresses which are set up in the joint between the body and the lid.

Typical Autoclave for Manufacture of Dye Intermediates.

A typical large-scale autoclave for the manufacture of dye intermediates may have an internal diameter of 3 ft. 6 in., an internal depth of 4 ft., being provided with a 6-in. charging hole and

a 2½-in. blowing orifice. Made of cold blast iron, 2½ in. thick, such an autoclave can be safely worked at a maximum pressure of 275 lb. per sq. in., if the temperature does not exceed 180° C., and under these circumstances the vessel may be filled (with the cold charge) to within 10 in. of the joint between body and lid. So charged, there is sufficient margin of safety for expansion, and the domed lid gives additional compression "head" for steam and ammonia resulting from the reaction.

With the maximum temperature and pressure specified, this autoclave can be used for the production of beta-naphthylamine, alpha-naphthylamine mono-sulphonic acids, Badische acid, Bronner acid, para-nitraniline ortho-sulphonic acid, and similar reactions. For higher temperatures and pressures, as in the making of beta-naphthylamine disulphonic acids, it is generally considered safer to use a cast-steel vessel.



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Fig. 2.—A HORIZONTAL MILD STEEL AUTOCLAVE FITTED WITH STEAM JACKET AND INTERNAL STEAM HEATING COILS ARRANGED TO FORM SHELVES FOR MATERIAL TO BE TREATED

Making and Breaking Joints.

The initial cost of an autoclave is high, as the "cooling-off"

and annealing is a skilled operation which may take several weeks to accomplish satisfactorily. It is therefore important to pay every possible attention to the question of care and maintenance. The faces of all flanges have to be very accurately machined to assist in giving a perfect joint, and in the case of the main joint between the body and the lid an annular groove is provided on the body flange to fit an annular spigot of slightly smaller size on the lid flange.

In addition, all of the bolts should be provided with nuts which are accurately machined to size, so that they may be tightened by the aid of a round steel box spanner with an hexagonal cavity which will exactly fit the nuts. Used with a hardened steel crossbar, such a spanner makes it possible to apply an even torque in the nut tightening or loosening opera-

tion, whilst the accurate fit of the nut and the spanner prevents the nuts from being distorted or otherwise damaged.

Use Asbestos String for Joints of Large Autoclaves.

For large autoclaves, which are provided with a charging hole, the main joint between the body and the lid is most effectively made with $\frac{1}{8}$ or $\frac{3}{16}$ -in. asbestos string, previously passed through a mixture of boiled oil and graphite. This impregnated asbestos string is wound in the form of a close-fitting spiral, so that it completely covers the bottom of the spigot groove in a single layer; the surface is then dusted with fine graphite and the lid is lowered into position and tightened up, the final tightening of the joint being done after the autoclave has been heated to 100° or 110° C. Such a joint will remain in good condition for at least twelve months, in the event of no earlier necessity arising for an official inspection of the interior of the vessel.

Lead Joints.

Soft lead is used for the main joint between body and lid only when this joint has to be frequently broken, as in the case of small autoclaves which are not provided with a charging hole. Such lead joints, as provided by a ring of soft lead, or by pouring molten lead into the spigot groove, require very considerable pressure on the bolts in order to be perfectly satisfactory, but even then they are liable to leak if the lid of the autoclave becomes distorted.

Joints at Charging Hole and Blowing Orifice.

The joints at the charging hole and the blowing orifice are preferably made with compressed asbestos-graphite composition sheet of good quality, $\frac{1}{16}$ to $\frac{3}{32}$ in. thick, cut to the requisite size. This jointing should be firmly fastened to the removable flange by smearing it with a coating of boiled oil and graphite; it is prevented from sticking to the flange on the autoclave body by a thin coating of vaseline and graphite, the clean metal surface of the flange in the latter case being dusted with fine graphite. Such a joint should serve about twenty times before it has to be renewed.

Packing the Gland Cavity.

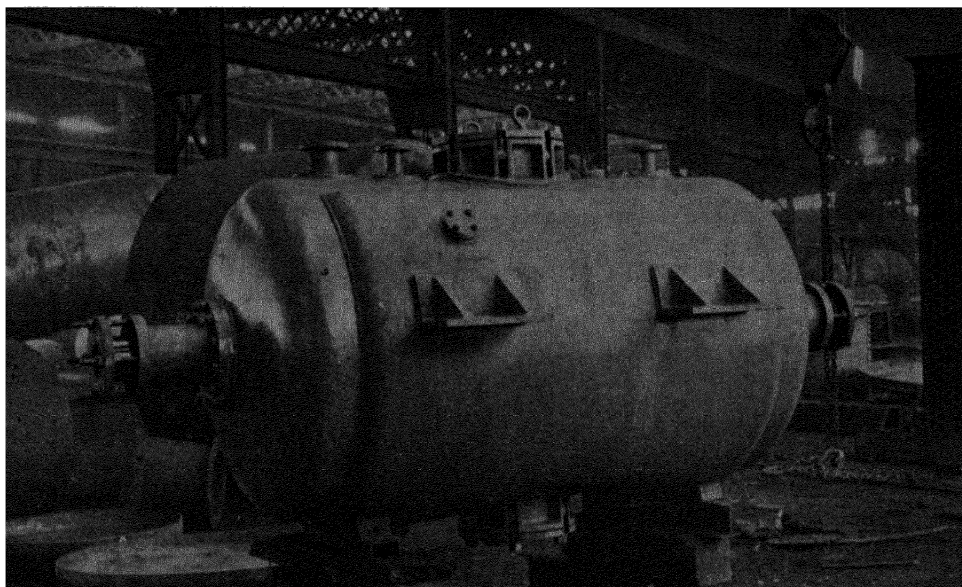
The packing of the gland cavity is a matter which demands very great care, otherwise it will be difficult to maintain a gas-tight condition when the autoclave is in operation. In the first place the cavity and the gland must be of ample dimensions, properly and correctly proportioned, the base of the cavity and the underside of the gland being dome-shaped. Secondly, there must be a good running fit where the stirrer shaft passes through the gland and the autoclave lid, mathematical exactness in boring the gland and lid and in turning the shaft being very essential if troubles are to be avoided.

Metallic packing made from antifriction lead alloys is the only type of packing which is suitable for the gland cavity where processes involve the use of ammonia or caustic soda under pressure. The alloy which is used must be of sufficiently high melting point to prevent it becoming soft at the maximum temperature of the autoclave operation. Shredded metallic "wool" is very easy and simple to fit, and if small tufts of it are evenly packed in the gland cavity, and well interspersed with graphite powder of good quality, a reliable joint is obtained. This "wool," however, has one disadvantage in being gradually compressed to a rock-hard mass and may be difficult to remove when it becomes necessary to repack the gland.

Plaited metal "rope" of square section, with a core of hard rubber or asbestos, is an alternative material. This "rope" is chosen for size to give a good fit in the gland cavity, and is inserted in the form of three flat rings which are accurately shaped from a straight length. Powdered graphite is dusted into all the loose crevices in the uncompressed rope and a good layer of graphite is placed between each ring when inserting it in the cavity.

Speed of Stirring.

The risk of an involuntary stopping of the stirring gear, and consequent settling or burning of the charge, is minimised by providing a reliable and non-slipping for power transmission. On large autoclaves, however, pulleys and belts are preferably replaced by a silent drive, which is still more satisfactory for autoclaves operating under high pressure conditions. The ne-



J. Thompson (Dudlev), Ltd.

Fig 3 —A MIXER TYPE OF JACKETED AUTOCLAVE

The body portion was water gas welded and then " stress relieved " in a special furnace at 650° C. The mild steel jacket was then welded on, as also were the various pads and other fittings

stirring, with a stirrer shaped to the contour of the vessel, should be such that the extremities of the stirrer move round the internal surface of the walls at a linear speed of 11 to 14 ft. per minute; the higher rate will be quite adequate to prevent any tendency for the charge to settle out, with the consequent troubles of localised burning. This is equivalent to a speed of 28 to 35 r.p.m., for an autoclave of 3 ft 6 in. internal diameter.

Discharging the Product.

The finished charge may be withdrawn from the autoclave by way of a blowing orifice and valve which is located at the bottom of the vessel; this arrangement, which is the most reliable, provides for an almost complete discharge if the orifice is placed as near as possible to the centre of the hemispherical bottom of the vessel, although precautions are needed to avoid the blockage of such an orifice by part of charge becoming semi-solid or charred.

Alternatively, discharge may be effected through a hollow stirrer shaft which is fixed to its lower part and is provided with a valve above the driving gear; this is not so reliable if the contents of the autoclave remain perfectly fluid

throughout and at the end of the reaction, but where there is any tendency for the charge to solidify or turn pasty this type of discharge is not so suitable. As a further alternative, the contents of the autoclave may be allowed to cool down so that they can be pumped out or syphoned out, after the stirrer has been stopped and the cover of the charging hole has been removed; this method causes considerable delay in manufacturing operations, although it is widely used where very high pressures are necessary in the autoclave reaction.

The Blowing Orifice.

Cast steel valves are essential for the main blowing orifice and the blow-off or pressure release. These valves should be secured direct to the autoclave body and lid respectively. In the case of direct-heated autoclaves it may be necessary to protect the blowing orifice valve against excessive local heat by providing a metal box of suitable shape, which can be loosely filled with asbestos wool and retained in position by an adjustable tripod or bracket for the duration of the heating operation and easily removed when the product is to be discharged. Spare valves, with

flanges correctly drilled, should be kept in stock so that they can be changed periodically, as it often becomes necessary to clean these valves and to regrind and repack them. Heavy-gauge solid-drawn mild steel tube, bent to shape, can be used to connect the blowing orifice valve to a point which is clear of the autoclave. This pipe must be effectively lagged with asbestos rope, and provision should also be made for heating it prior to blowing the charge. This heating may be done very conveniently by fitting a steam inlet close to the valve; such a steam inlet will also serve to keep the pipe clean, if used regularly after the blowing of each charge.

Pressure Gauge and Thermometer Pocket.

The pressure gauge should register 50 per cent. more than the maximum reading normally required. Steel tube gauges must be used, especially as ammonia or caustic soda often enters into the autoclave reaction or become evolved during the reaction. The gauge should be provided with an ample length of thread on the connecting socket so that it can be well screwed upon the syphon tube and locked in position by a back nut. Unless this particular joint is made and maintained in an absolutely gas-tight condition, no reliance can be placed on the readings of the gauge; at the same time troubles may arise by distillates (ammonia, naphthylamines, etc.) passing through the seal in the syphon tube. Each leg of the syphon tube should be 6 to 8 in. in length in order to allow for ample movement of the column of mercury, and the mercury should be protected at each surface level by a small quantity of thick mineral oil.

For large-scale autoclaves the syphon tube should be of solid-drawn mild steel tube, $\frac{3}{8}$ -in. bore and 1-in. external diameter, and the end which is screwed into the autoclave cover must be accurately threaded so that a good joint is obtained.

Similar precautions apply to the thermometer pocket, which can be made from steel tube of the same dimensions, sealed at the bottom by a long plug and welded over, whilst the top is provided with a welded-on hexagonal-headed fitting to enable it to be screwed into the lid of the autoclave. This pocket, moreover, must be sufficiently long to reach well below the surface of the liquid charge, or faulty

readings will be obtained. In use the cavity between the thermometer and the walls of the pocket is filled with either mercury or oil.

Gas Burner Precautions.

In direct heating by a ring-shaped gas burner care must be taken to see that the centre of the hemispherical base of the autoclave, to a radius of 9 in. or so (for a 3 ft. 6 in. vessel) is left quite free from the direct play of the flames, for at this point the agitation of the charge is at its slowest rate, and there is a much greater risk of burning and of scale formation. The burner holes immediately below the blowing orifice should also be modified or sealed to avoid excessive local heating of the valve and its lagging. Where high-power burners are employed, with a rotary blower feeding gas at a pressure of 6 to 8 lb. per sq. in., it is a wise precaution to provide a small pilot jet to each burner unit to avoid the risk of explosion when lighting up. Long handles to all gas valves will allow the flame to be easily adjusted.

Exothermic Reactions.

Special precautions must be taken in operating the autoclave where the reaction is exothermic, for even if the final temperature and pressure due to a sudden generation of heat is not exceptionally high, the suddenness of the increase is liable to strain the vessel and its fittings. Reactions which may be exothermic should be tried out in an experimental autoclave, in order to find the approximate minimum temperature at which the evolution of heat will commence. Safe working is then possible, for burners can be immediately extinguished (or steam can be shut off) as soon as the requisite temperature is reached.

The production of para-nitraniline ortho sulphonic acid is a typical exothermic reaction. Here the burners can be put on until the temperature reaches 132°C with a pressure of 160 lb. per sq. in., and half-on for another 15 minutes until the temperature becomes 137° and the pressure increases to 175 lb. Being completely extinguished, the temperature during the next three periods of 15 minutes will automatically go to 140° (185 lb. (194 lb.), and 149° (220 lb.), and fall to 148° (205 lb.), at which burners are relighted.

PAINTS AND VARNISHES

PART VII.—SPIRIT VARNISHES AND PAINTS

By H. COURTNEY BRYSON

SPIRIT varnishes are distinguished from oil varnishes by being simple solutions of gums and resins in a volatile solvent. On evaporation the resin is deposited as an adhesive continuous film. No chemical action in the way of oxidation or polymerisation is involved.

Chief Resins Used.

The chief resins used are shellac, rosin, spirit soluble copal, dammar, mastic and sandarac as well as many synthetic resins, such as rosinol (non-active phenol-formaldehyde resin) and albertol. The principal solvents are alcohol, ethyl alcohol, acetone, white spirit and to a lesser extent many of the solvents used in the preparation of cellulose lacquers.

French Polish.

This is probably one of the oldest spirit varnishes known. It is commonly composed of 60 lbs. of finest pale orange shellac dissolved in 24 gallons of 64 O.P. industrial alcohol. Since shellac contains complex organic acids such a solution should be packed in jars of stone or glass, not in metal containers. In order to reach any solution which has darkened on this cause or any other and in order to get the palest possible results, about 1% valic acid is often added to the French polish. Such an addition is also claimed, assists in the

polishing of the wood. Further additions of sandarac, benzoin, mastic and even rosin are often made in order to obtain special effects or a reduction in price. Shellac contains about 5 per cent. of wax, or, rather, of two waxes which are insoluble in alcohol. These waxes render the alcoholic solution cloudy. For French polish this is not only desirable but necessary.

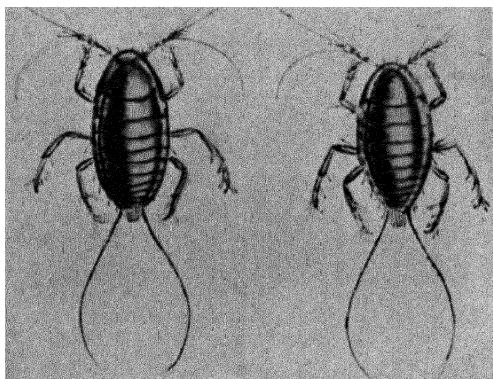
Application of French Polish.

The polish is applied by hand to wood, lightly oiled with linseed oil, by means of a rubber, i.e., a piece of old soft linen, folded many times to form a pad and saturated with the shellac polish. If a wax-free polish were used then the rubber would drag

and not even oiling with a tiny drop of olive oil would cause it to work properly. The application of French polish needs skill and energy.

The Examination of Shellac.

The complete technical examination of shellac is seldom necessary, but since it is an expensive material and very widely used—32,000 tons being exported annually from India—it is always liable to adulteration. This is less true now than in days gone by but, nevertheless, being a natural product produced largely by unskilled native labour in a far-away land it lacks uniformity. In fact, the more important users of lac have taken the step of importing the raw seedlac and themselves



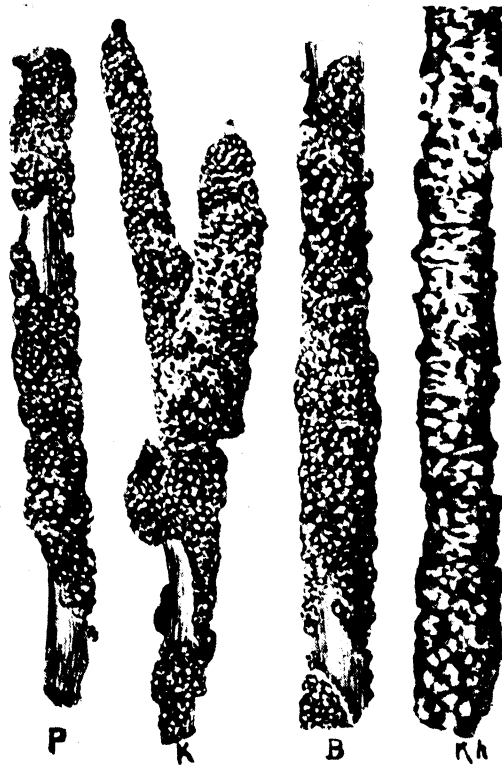
Indian Lac Cess Committee
Fig 1.—LAC INSECTS GREATLY ENLARGED.
Lac is an animal product secreted by a tiny insect .05 of an inch long

making it up in the various grades of lac which are employed in industry, so that to-day over 25 per cent. of the Indian exports are in the form of seedlac.

Lac is unique in that it is an animal product secreted by a tiny insect .05 inch long living on a tree-branch, from which it never moves, by sucking the sap. Vast numbers live and suck side by side, their resinous excretion forming a solid coat on the branch. On their death the young ones crawl out from the body of the mother through the breathing tube stuck up through the lac coating. This coating is sticklac.

How Shellac is Obtained.

In India the twigs are collected, ground, sifted, winnowed, washed, by native treading, dried and converted mostly to shellac and button lac by mixing with powdered orpiment and sometimes with as much as 10-12 per cent. of rosin. The lac is filled



Indian Lac Cess Committee

Fig. 2.—STICKLAC.

Showing the formation of the various depositions. P, Palas; K, Kusmi (the most highly prized); B, Ber; Kh, Khair.



Fig. 3.—SURFACE OF A PIECE OF STICKLAC GREATLY ENLARGED.

Showing holes formed by the breathing tubes of the lac insects.

into long linen bags held in front of a charcoal fire and twisted from either end. As the molten lac squeezes through it drips on to a moistened stone slab.

Button Lac.

Button lac is made by lifting small amounts of the molten resin from the surface of the bag and allowing it to fall on sheet tin on which it spreads out like a little pancake. It is then stamped with a mark. The familiar flakes are produced by seizing a lump with hands, feet and teeth and stretching outwards and upwards to form a large, thin sheet which is broken up.

Garnet Lac.

A large and increasing proportion as already indicated is prepared mechanically by solvent extraction or by steam heating, giving a more uniform product. One of these grades is known as mechanical Garnet lac. Germany has been particularly successful in

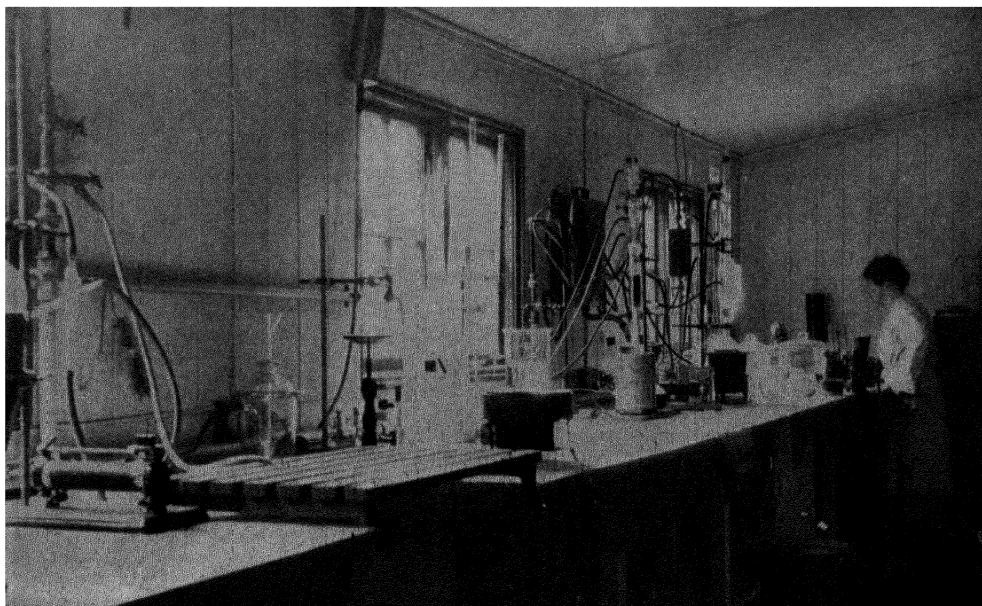


Fig 7—LAC RESEARCH AND TESTING LABORATORY

Indian Lac Cess Committee

Showing apparatus for estimation of amount of wax and insoluble matter in shellac, as well as apparatus for performing fluidity and life under heat test.

For example, taking the iodine value of shellac at 16 and the iodine value of rosin at 228, the percentage of rosin in a TN Orange shellac with an iodine number of 33.9 would be:—

$$\frac{100 (33.9 - 16)}{228 - 16} = 8.5 \text{ per cent.}$$

Effect of Storage on Shellac.

Lac loses weight and becomes increasingly insoluble in alcohol on ageing. Roughly 2 per cent. solubility is lost per annum. Correspondingly there is a rise in acid value and more alkali is required to dissolve a given weight of old shellac. The graph shows the loss in solubility on heating to 120° C. Shellac in this condition is termed "dead," or perished. It has recently been discovered that depolymerisation may be effected by treatment in an autoclave restoring the lac to practically its original "lively" condition. The process has not yet been commercially exploited though it is to be anticipated that this will not be long delayed since it is not uncommon for whole shipments to arrive in this country in an almost insoluble and worthless condition.

Brown Hard Spirit Varnishes.

These are used in enormous quantities

as cheap brushing lacquers, especially in the furniture trade. A typical recipe consists of:—

Garnet Lac	..	..	80 lbs.
Rosin	..	..	40 lbs.
Methylated spirit	..	..	40 galls.

Knotting.

This is a spirit varnish used to seal knots in wood to prevent the resin contained in them from bleeding through and affecting subsequent coats of paint and the like. A really good quality white knotting would consist of 60 lbs. of white lac dissolved in 12 gallons of industrial methylated spirit.

Copals.

Certain varieties of the softer copals are almost wholly soluble in alcohol. These varieties are sought after for the manufacture of spirit varnishes. Moderate heat treatment or mastication of rollers increases the solubility of copals. Unfortunately copal solutions are inclined to be stringy, especially just before drying is complete. Solubility is greatly improved and stringiness lessened by using a mixed solvent and by employing an acidic body like rosin to help disperse the difficultly

soluble portion. A solution made on the lines indicated is generally allowed to stand for some time in order that all insoluble matter—sand and bark from the tree as well as mucilaginous matter—may settle out.

Method of Solution.

The method of solution for most spirit polishes consists in putting the solids and the solvents into an eccentrically mounted rotating barrel and allowing it to revolve for a long period till solution is complete. Coarsely powdered glass is often placed in the barrel before the solids are added in order to prevent agglomeration into a solid mass which would be very slow to dissolve. The old-fashioned method of tumbling in a barrel and then allowing to settle gives better and cheaper results than attempting to dissolve with the aid of heat and filter-pressing to clarify.

Testing for Impurities in Copal.

Impurities in copal can be tested in the following simple manner. Weigh out 10 gm. of the finely powdered copal into a tared conical flask and add 50 c.c. of a solvent composed of 25 c.c. of amyl acetate, 50 c.c. of amyl alcohol and 40 c.c. of ethyl alcohol. Allow to digest with constant stirring on a water bath. When all the impurities are freely separated, decant the clear solution, rinsing out the flask three times with the solvent. Evaporate both the residue and the decanted matter (for purposes of checking) and express the result as a percentage.

Dammar Spirit Varnishes.

These are considered inferior to the best copal varnishes. They are generally more brilliant, paler and freer from string. Their weather-resisting properties are very

bad and they do not always dry well. They are mostly used, dissolved in white spirit, to produce what are known as white crystal paper varnishes for wall papers and the like. The usual steps regarding stirring and settling are carried out.

Gloss Oil.

Rosin alone, or calcium rosinate dissolved in a cheap solvent such as duty-free (heavy) petroleum distillate, is known as gloss oil and is used for imparting a finish to cheap toys and cheap furniture. It becomes tacky on handling and has no durability. A slightly better formula is comprised of 90 lbs. of W.W. rosin dissolved in 10 gallons of mineral naphtha with the addition of 10 lbs. of dammar.

Sandarac.

This also produces a suitable varnish for paper, labels, cardboard and wood. For example, 5 lbs. of sandarac are dissolved in 20 lbs. of alcohol and 3 lbs. of

burgundy pitch are added to give flexibility.

Mastic.

This is a fine white gum coming from Chios in the form of hard tears, though an inferior quality comes from Afghanistan. It is used, often in conjunction with sandarac, copal or lac, in the very finest quality of spirit varnishes. It has the following characteristics.

Acid value, 59.

Saponification value, 82.

Soluble in chloroform, ether, xylol, toluol, etc.

Insoluble in water.

Partly soluble in alcohol and turpentine.

Yacca, Accroides.

Grass-tree, or Botany Bay gum as it is

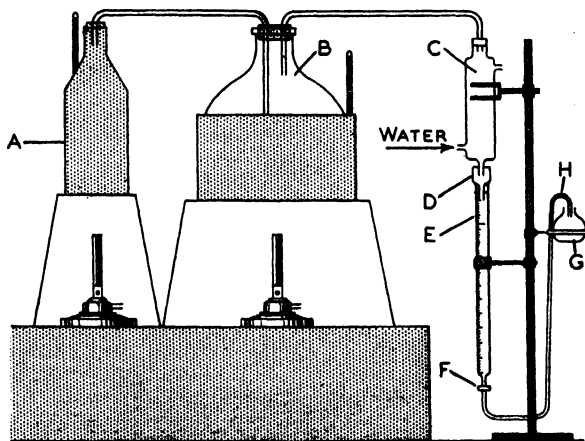
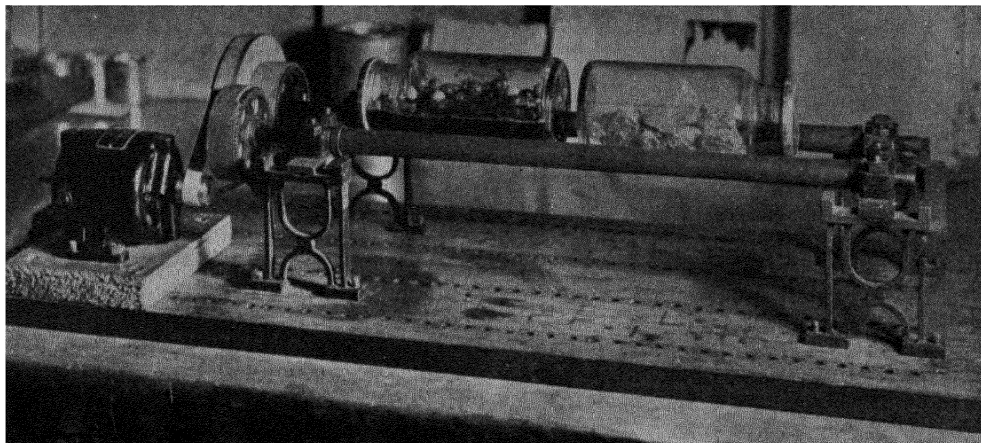


Fig. 8.—APPARATUS REQUIRED FOR THE STEAM DISTILLATION TEST.



THE MANUFACTURING CO., LTD.

Fig. 9—LABORATORY MILL FOR GRINDING PIGMENTS IN MEDIA

The whole is placed in an hermetically sealed bottle, together with some marbles, and rotated. Excellent grinding results. This apparatus may also be used for dissolving gums, etc., as shown by the bottle on the right.

variously termed is a product of the *Xanthorrhoea*, only two members of which family yield gums. Red accroides is the variety which usually appears on the market and it has very useful properties, which are not generally appreciated. It contains phenols and resembles shellac in some ways.

Japanese Lacquer

contains a compound called *urushiol* of phenolic nature and dries to a hard, tenacious, adhesive and insoluble film on exposure to moist air. Much research has been done on this lac by Japanese scientists. The method of application apparently needs considerable skill and the services of a menagerie. Quin states that the design is traced on paper with a rat-hair brush and the paper applied to the article with whalebone. The parts are then gilt with a hare-hair brush, the excess of metal being removed by a brush made from the long winter hairs of a white horse. The final rubbing down is done with camellia wood charcoal.

Spirit Enamels.

These are made, just as in the case of oil paints, by grinding in the appropriate pigment to the medium. The most usual method of doing this is by means of a ball mill. An inexpensive laboratory mill is shown in Fig. 9. The whole of the ingredients are placed in an hermetically sealed bottle and this is laid between

two rubber-covered rollers which rotate in the same direction and drive the bottle by friction. Different speeds are obtainable by the simple process of using a bottle of different diameter.

It is sometimes more expedient to grind the pigment into the plasticiser, in which case a triple roll mill is employed. The resulting paste is mixed with the solution of spirit varnish in a high speed mixer.

Examination of Spirit Varnishes and Lacquers.

Lacquers must be separated into pigment and medium. This is probably best done by dilution and settling.

The recognition of the solvents is best achieved by steam distillation, using the apparatus shown in Fig. 8.

Steam Distillation Process.

The substance to be steam distilled is placed in the flask B and heated while steam from the container A is blown through it. The vapours are condensed by the condenser C and pass by means of the not quite air-tight connection D into the burette E. When the burette becomes too full of condensate the cock F is opened, which allows the aqueous portion to run via the tube H into the container G, when in the event of no water-soluble matter being present it is rejected. The amount of non-miscible and lighter-than-water

material is read off from the burette and then run out to be examined in the usual way.

The water soluble solvents are recovered from the aqueous distillate by salting out with potassium carbonate, and tested in the usual manner for alcohols, esters, aldehydes, ketones. Reducing substances such as turpentine, alcohols, esters, as well as some ethers, may be easily recognised by the fact that on boiling with a solution of potassium bichromate in 25 per cent. sulphuric acid a green coloration is produced.

Esters are present if a small quantity of alcoholic potash refluxed with a portion of the solvent (after neutralisation) remains colourless to phenolphthalein.

Identification of Gum.

The gum is always a difficult matter to identify with certainty for it is usually a mixture. Its appearance and general characteristics will afford valuable clues. It should be remembered that shellac is very sensitive to alterations and that steam distillation will affect it. In fact, the solvent after distillation will generally smell quite strongly of shellac. The solubility of the residue in carbon bisulphide, ether, acetone, methyl alcohol, benzene, turpentine and chloroform will also help. Glacial acetic acid may be used as a test for mastic as that is the only natural resin insoluble in the reagent. A table of solubility of resins should be consulted, though it must be remembered that the figures given by such tables are susceptible to the widest variation for individual samples of the gum. The acid value should be taken by refluxing with equal parts of benzene and alcohol while the iodine value will also often give confirmatory results.

Hirschsohn's Analysis of Natural Resins.

An elaborate scheme of analysis for natural resins has been worked out by Hirschsohn using a series of specially prepared reagents which give colour reactions with the following groups:—

- (1) Completely soluble in chloroform:
 - (a) Completely soluble in ether;
 - (b) Imperfectly soluble in ether.
- (2) Imperfectly soluble or insoluble in chloroform:
 - (c) Completely soluble in ether;
 - (d) Imperfectly soluble in ether.

The Halphen-Hicks Reaction.

The Halphen-Hicks reaction is also very useful. This is performed in the following manner. A few drops of a solution of one part of phenol and two parts of carbon tetrachloride are added to a solution of a small portion of the gum in carbon tetrachloride. A drop of the mixture is placed on a white tile and a ring of solution composed of one volume of bromine and four volumes of carbon tetrachloride is drawn round this drop with a glass rod, care being taken that no mixing takes place. The bromine vapour slowly passes across the gap and produces a characteristic colour with the gum under examination. If rosin is present its colour is generally so intense that the other colours are masked. A blank should always be run with a sample of the resin the presence of which is suspected.

Rosin.—Green, which rapidly changes first to blue and then to violet, which in turn, slowly fades, changing to purple and very deep blue.

Shellac.—Gives no colour change when quite pure, but since most lacs contain rosin the above reaction may be expected. Some pure dewaxed lacs give a faint brown-yellow colour.

Dammar gives a brown colour which slowly changes to a reddish-brown and then a deep crimson.

Manila Copal slowly forms a faint, dirty green, which slowly goes first violet then purple.

Sandarac.—Persistent lilac almost at once which gradually becomes deeper in hue, changing to violet-brown furthest from the bromine.

Mastic.—Reddish-brown and carmine near the bromine and a much paler brown remote from the bromine.

Kauri becomes first azure blue and then rapidly darkens to purple. Remote from bromine appears dark olive.

Elemi gives an intermediate indigo which gradually deepens to deep indigo and possibly purple.

Zanzibar Copal.—A light brown slowly forms, becoming chocolate and violet.

Identification of Synthetic Resins.

Since synthetic resins are now sometimes used in some of the more expensive types of spirit polishes and lacquers in order to obtain special effects, a few notes setting out some of the simpler tests

which may be applied to the recognition of synthetic resins will be useful. These consist (a) of heating the resin either in a hard-glass tube or on a piece of broken silica in a bunsen flame; (b) of fusing with soda lime; (c) of fusing with sodium as in the ordinary way of organic analysis in order to recognise the elements N, S and halogens and (d) of saponification. The complete separation of all the possible products of the saponification of all types of synthetic resins involves several extractions with petroleum ether, ethyl ether and the like and is a lengthy procedure. Further information will be found in the articles on Synthetic Resins.

(a) Heating Alone.

Phenol Formaldehyde Resins may be recognised by a very characteristic odour when burnt, strongly reminiscent of phenol.

On boiling with 10 per cent. caustic soda, acidifying with hydrochloric acid, filtering and adding bromine water to the acid filtrate, precipitates of the bromphenols are obtained.

Coumarone Resins.—May be identified also by their characteristic smell on heating. The Liebermann-Storch reaction results in a deep rose-pink colour. Dammars also give this colour.

Urea Resins on burning give rise to a mixture of amines with a very disagreeable and characteristic odour. The vapours have an alkaline reaction to litmus.

Alkyd or Glyptal Resins on heating in a tube with potassium bisulphite give a sublimed ring of phthalic anhydride. If glycerine were the polyhydric alcohol used in the manufacture, acrolein is also evolved (readily recognised by its unpleasant effect on the eyes).

Vinyl Resins on heating in a dry tube give rise to acids depending on the nature of the original ester employed, e.g., vinyl acetate gives acetic acid and so on.

Acetaldehyde Resins on heating in a closed tube give off acetaldehyde, which is readily recognised by its odour and may be confirmed by obtaining a red coloration with Schiff's reagent.

Ester Gums in general give the same colour reactions as the rosin from which they are derived.

(b) Heating With Soda Lime.

This is a useful test for resins.

Coumarone resins evolve an odour of a mixture of diphenyl and naphthalene.

Phenol-formaldehyde resins readily evolve phenol which may be recognised by its odour. Confirmation is obtained by dissolving the fused mass in water, saturating with carbon dioxide and extracting the phenol with ether.

Cyclohexanone resins evolve cyclohexanone which is easily identified by its odour.

Acetaldehyde resins give a copious yield of acetaldehyde.

Vinyl resins also give rise to the evolution of acetaldehyde on heating with soda lime.

(c) Fusion With Sodium.

This together with testing in the ordinary way for sulphur and nitrogen will indicate a urea or a thiourea resin, according to whether one or both of the elements named be present. Traces of nitrogen may be derived from a nitrogen-containing catalyst in some other variety of resin.

Chlorinated phenol resins give the halogen reaction.

Sulphonamide resins also show positive tests for nitrogen and sulphur.

Vinyl chloride resins will also react positively to the halogen test.

(d) Saponification.

This is one of the most valuable tests for synthetic resins.

Coumarone, styrene and acetaldehyde resins are unsaponifiable.

All the other types of synthetic resin saponify to yield products which may be identified with more or less certainty.

Acidification and steam distillation of the dried residue will produce in the distillate, aldehydes which may be readily recognised by Schiff's reagent (rosaniline-hydrochloride solution just bleached with SO_2). If formaldehyde is found, the presence of phenol, cyclohexanol, urea or sulphonamide resins is indicated.

Acetic acid indicates the presence of vinyl acetate resins. Phthalic acid, citric acid, maleic acid, malic acid, succinic acid, generally indicate the presence of alkyd resins though sometimes these compounds are used to modify phenol resins.

CHOCOLATE MANU- CONTROL

PART II.—SCIENTIFIC CONTR.

TWENTY years ago only one or two of the larger confectionery firms included a chemist on their staff, but nowadays practically every leading manufacturer possesses a well-equipped laboratory to deal with the various problems arising during the course of manufacture. In addition, most firms subscribe to the Cocoa and Chocolate Research Association, which has done valuable fundamental work on the basic problems of the industry. The work of the chemist in the chocolate industry may be divided into three phases :—

(1) Analysis of Raw Materials.

Nowadays this includes, in addition to the basic ingredients of chocolate, a wide variety of products ranging from fuel oils and lubricants to wrapping papers and silk ribbons.

(2) Factory Control.

Adherence to recipe is checked by analysis of samples of the finished and partially finished product. Efficiency of refining is controlled by microscopic measurement of the size of the sugar particles. Keeping qualities of the goods are examined by storage tests under controlled conditions of temperature and humidity.

(3) Research.

In these days of extensive competition there is always a need for research work in order to improve processes and recipes and overcome technical difficulties. A chemist in any industry must not be content to remain solely in his laboratory ; he must go out into the factory to obtain a thorough insight into the various stages of manufacture and collaborate with the manufacturing and engineering sides of the business in any investigational work.

Analytical Control of Raw.

The scope of this article is one which will only permit dealing with the main ingredients of chocolate.

Selection of Cacao Beans.

The selection of cacao beans is primarily a matter of experience and it is extremely difficult to lay down hard and fast rules. An attempt is made in the Table on page 1382 to indicate the various characteristics of some of the more important varieties, and the following points should be noted in the examination of a parcel of beans :—

Extent of Fermentation.

Properly fermented beans generally have a shell which is free from pulp and easily removed, and on cutting show a rich, dark characteristic colour. Poorly fermented beans have a tougher shell which is difficult to remove, the kernel is greyish in colour and lacks aroma. Over-fermentation renders the shell brittle and easily broken.

Freedom from Mould and Insect Infestation.

The presence of mould should be noted and avoided, since it gives rise to a musty flavour.

Cacao beans are extremely liable to infection with the so-called Cocoa Moth (*Ephestia elutella*). Any signs of webbing, larvæ or actual grubs should be carefully noted and the percentage of infected beans estimated. Badly infected samples should be immediately burnt to prevent infection of the factory premises, since although this pest is entirely eliminated from the raw material, by the various cleaning, roasting and manufacturing processes which it undergoes, there is always a chance of a stray moth re-infecting the finished product.

CONTROL

BEANS.

		Characteristics of		Flavour.
		Shell.	Nibs.	
	..	Hard, light brown.	Dark purplish brown.	Earthy and bitter—little aroma.
	Large, but flat and irregular (19/20).	Light brown ..	Dark outside, lighter inside, high fat 54 per cent.	Spicy and scented.
	.. Small, irregular and flat (26/28).	Greyish ..	Dark brown to violet.	Acidic, bitter, smoky.
	E. Venezuela	Flat and small (23/25).	Dark	Astringent to bitter.
	Ceylon ..	Round and plump (21).	Smooth, clean, thin, light brown.	Mild and sweet if properly fermented, astringent if badly fermented.
Maracaibo ..	Venezuela ..	Large, plump and irregular (18/19).	Smooth, red-brown.	Red brown, 50/52 per cent. fat.
Para ..	Brazil ..	Fairly plump, small (25/27).	Red brown ..	Chocolate brown to purple.
Puerto Cabello	Venezuela ..	Large, full and plump (20/21)	Reddish-brown, generally covered with brown clay.	Rich brown, 49 per cent. fat.
Trinidad ..	W. Indies ..	Flat and broad (23).	Dark red brown, smooth.	Red brown to violet.
				Pronounced and good chocolate flavour if properly fermented.

Aroma.

If the beans are crushed and rubbed between the hands the aroma and traces of acidic unpleasant odours can be detected, but here again considerable experience is necessary in evaluating the worth of the beans.

Shape and Size.

The characteristic shape and appearance of the bean is noted and the size can be judged by estimating the number of beans to the ounce by counting a weighed amount (4—8 ozs.) of the beans.

Amount of Shell and Germ.

A weighed amount of beans from the buying sample is carefully shelled by hand and the germ extracted, the separated nibs are then reweighed and the percentage of shell and germ calculated. These results are checked on delivery of the main consignment by the actual

figures returned for shell, germ and nib after the roasting and winnowing processes, due allowance being made for the loss in moisture during roasting.

Percentage of Water.

A weighed amount of the bean is roughly broken up, dried in a steam oven for three hours to constant weight and the percentage of water lost calculated.

Percentage of Fat.

The average fat content of the nib is 50 per cent., but in some varieties the fat amounts to 56 per cent. and, therefore, its determination is of importance.

The method used is described in detail later under chocolate analysis, but with nibs the process is distinctly longer and the sample must be frequently ground down with clean, dry sand in a pestle and mortar to thoroughly disintegrate the vegetable tissues.

Sugar.

The modern methods of refining sugar produce an extremely pure product containing 99.95 per cent. of sucrose. For chocolate manufacture, as long as the sugar contains 99.7 per cent. or over of sucrose it does not matter if its colour is a shade below that of the highest grades of sugar which are needed for other confectionery work.

The purity is determined by using a polarimeter. With a Schmidt and Haensch instrument, a solution of 26.05 gm. of the sugar is made in cold distilled water and the final volume adjusted to 100 c.c. The solution is introduced into a polarimeter tube 20 cm. long and the angle of rotation taken from an average of several readings. In some instruments the percentage of sucrose is read direct on a Ventzke sugar scale, but if this is not present, it is only necessary to divide the observed angular rotation by 0.3466 to obtain the percentage of sucrose, provided always that exactly 26.05 gm. have been weighed out and a 20 cm. tube used.

The percentage of invert sugar should be determined if the polarisation figure is on the low side and should not exceed 0.2%.

The cleanliness of the sugar used is, of course, an important point to watch, although little fault can be found nowadays with sugar from a reputable source.

Sifting through a sieve and solution in water are two obvious methods of detecting the presence of foreign matter such as string, sack fibres, etc.

Finally, since sugar is treated with various chemicals during its refining, it is essential to test it for possible contamination with arsenic by a Gutzeit or a Marsh-Berzelius test, described elsewhere. Here again sugar from a reliable source will have been carefully tested for possible contamination before it reaches the user.

Cocoa Butter.

The various analytical tests which are applied to cocoa butter have been described in full detail earlier in the work. In addition to these tests, which indicate its purity, it is essential that the cocoa butter should have a good aroma, possess a mild chocolate flavour, and be hard and close in texture.

The observer should be on the look-out for harsh smoky or acidic flavours, but at the same time flat, tallowy or weak

flavours are also to be condemned. Cocoa butter is an extremely stable fat and rancidity is rare, but its development is accelerated if the cocoa butter contains moisture in excess of 0.1 per cent.

EXAMINATION OF THE FINISHED CHOCOLATE.

The following tests should be carried out :—

Fineness of Grinding.

A portion of the chocolate is roughly flaked off with a pen-knife, introduced into a test-tube and well shaken with dry petroleum ether (40-60). The mixture is allowed to settle and the supernatant ether which contains most of the fat poured off. The remaining suspension of chocolate in ether is again shaken, a thick glass rod dipped into the tube and a smear of chocolate made on a microscope slide. A cover-slip is mounted in canada balsam over the chocolate and in this way an excellent microscopic preparation is obtained which can be examined and kept for future reference.

The examination is usually carried out under a 1-in. objective, using a micrometer scale in the eyepiece of the microscope, which has been previously calibrated against a stage micrometer. Most of the particles will be extremely small and, of course, the standards of fineness required vary according to the grade of the product, but as a general rule the largest sugar crystals should not be more than 0.0015 to 0.002 in. long for a quality article.

When examining the size of the sugar crystal it is convenient to work under crossed nicols (polarised light), as this enables the crystals to be picked out with greater ease; the microscope, therefore, should be fitted with the usual polariser and analyser.

In actual manufacture these fineness examinations are also made on the unfinished chocolate as it comes off the refiner in order to check the effectiveness of the grinding at this important stage and make any necessary adjustments to the refiner. In this connection it has been found useful to project an image of the slide on to a screen for demonstration purposes to foremen and charge hands. This is done by illuminating the slide with a carbon arc and fitting a Zeiss reflecting prism attachment to the eyepiece of the microscope.

Moisture Content.

It is difficult to accurately determine the moisture in chocolate, but for routine purposes it is sufficient to rapidly weigh thin flakes of the chocolate in a shallow dish and heat the dish and its contents in an air oven at 100–105° C. for three hours.

Fat Content.

The fat content of chocolate is determined by extraction with petroleum ether in a Bolton and Revis fat extractor. A thimble is made by wrapping an 18.5 cm. No. 2 Whatman filter-paper round a test-tube of suitable size, introduced into the inner glass tube of the extractor, and the test-tube removed. About 5 gm. of finely flaked chocolate are weighed into the thimble and a weighed CO₂ flask is half filled with dry petroleum ether (40-60). The reflux apparatus is then connected up to a double-surface condenser and heated over an electric lamp or on a

Fig. 1.—BOLTON AND REVIS FAT EXTRACTOR.

water bath. After extraction for some 2 to 3 hours the source of heat is withdrawn, the thimble allowed to drain and its contents finely ground in a small pestle and mortar. The partially extracted chocolate is put back into the thimble and extraction repeated for a further hour.

After draining, the CO₂ flask is removed, the ether distilled off and the fat dried in a steam oven for some 30 minutes before reweighing.

Sugar Content.

The sugar content is determined on the dry fat-free material left after the fat extraction. Between 0.6 and 0.8 gm. of this fat-free material is weighed out into a small beaker, heated with about 20 c.c. of distilled water on a water bath. The suspension is then clarified by stirring in 1 c.c. of lead subacetate solution followed by 5 c.c. of sodium sulphate solution. The contents of the beaker are then filtered into a 100 c.c. flask, washing the precipi-

tated matter repeatedly with small quantities of warm water until approximately 80 c.c. of solution are collected in the flask. Then 10 c.c. of 6.34 N hydrochloric acid are added and the flask immediately immersed for 12 minutes in a water bath, the temperature of which is maintained at 60° C.

At the end of this period the flask is withdrawn, rapidly cooled, just neutralised with sodium hydroxide and the final volume adjusted to 100 c.c. The actual estimation of the invert sugar thus obtained is determined by a volumetric Fehling's titration.

Estimation of Sugar by Fehling's.

Fehling's solution is made up in two different portions.—

- | | |
|---|-------|
| (a) 69.3 gm. copper sulphate per litre. | |
| (b) 346 gm. of Rochelle salt | } per |
| 142 gm. of sodium hydroxide | |

Equal portions of these two solutions are mixed together and 10 c.c. of the mixture is pipetted into a conical flask and diluted with 60 c.c. of water. The contents of the flask are then brought to the boil (adding a few fragments of porous pot to prevent bumping) and the sugar solution run in from a burette.

When the blue colour of the solution has practically disappeared, three drops of 1 per cent. methylene blue solution are added, which produces an intense blue coloration. As the titration is continued this coloration then gradually changes through purple to crimson until on the addition of a final drop it turns to scarlet.

The solution is kept vigorously boiling throughout the whole process and the first titration is taken as a trial and the average of two subsequent titrations obtained.

Standardisation of Fehling's Solution.

The Fehling's solution is standardised by titrating it as above against a 0.5 per cent. solution of sucrose which has been similarly inverted with acid at 60° C. It will be found that 10 c.c. of Fehling's solution will require approximately 10 c.c. of the standard sugar solution, and the strength of other unknown solutions under test should be so adjusted that titrations of a similar magnitude are obtained. The factor for the Fehling's solution is thus obtained, that is, the weight of sucrose in grams equivalent to 10 c.c. of the Fehling's solution.

The percentage of sugar in the original chocolate is then obtained from the following data :—

If F = Factor of the Fehling's solution.

w = Weight of fat-free chocolate in 100 c.c.

t = c.c. of this solution used.

f = Percentage of fat in chocolate.

m = Percentage of moisture in chocolate.

Percentage of sugar

$$= \frac{F \times 100 \times \{100 - (f + m)\}}{t \times w}$$

Estimation of Sugar Content by Polarimeter.

The sugar content of a plain chocolate can also be determined by polarisation and, provided the polarimeter used is an accurate one, this is sometimes preferable, since there is always a possibility of some of the cocoa starch being converted to dextrose sugar during the inversion process with acid, thus giving high results. A solution of 10-15 grams of chocolate is made, cleared with lead subacetate and the excess lead precipitated with sodium sulphate. The solution is then made up to 100 c.c., filtered and polarised, due allowance being made for the volume of precipitated matter by running a duplicate estimation side by side, using only half the weight of chocolate first taken; the corrected first reading will be given by the product of the two readings divided by their difference.

Cocoa Content.

Having determined the moisture, fat and sugar content of a plain chocolate there remains the fat-free cocoa matter, which consists of a complex mixture of various compounds. A close approximation of its percentage, however, is

obtained by determining its nitrogen content by the Kjeldahl process and multiplying the percentage obtained by 20.

Approximately 1 to 1.5 gm. of the chocolate are weighed into a Kjeldahl flask and 10 gm. of powdered potassium bisulphate, 25 c.c. of pure concentrated sulphuric acid and a small crystal of copper sulphate added. The flask is heated in a fume-cupboard until all organic matter has been destroyed and a clear pale green solution remains.

This is transferred to the distillation apparatus, rendered alkaline with caustic soda solution, and the ammonia thus formed is distilled into 25 c.c. of N/10 sulphuric acid. The acid is subsequently back-titrated with N/10 sodium carbonate solution using methyl orange as indicator. A blank experiment is carried out side by side using the same reagents.

Then if :—

w = Weight of chocolate taken.

a = c.c. of N/10 acid used up by the chocolate.

b = c.c. of N/10 acid used up by the blank.

Percentage of fat-free cocoa matter

$$= \frac{14 \times (a - b) \times 100 \times 20}{10,000 \times w}$$

In this way the complete analysis of a chocolate is obtained and by suitable calculations it can be transcribed into an actual working recipe of nibs, sugar and additional cocoa butter.

Milk Chocolate.

A milk chocolate presents a much more difficult problem to the analyst and it is essential in addition to determine the lactose, Reichert-Meissl value of the fat and the calcium content of the ash before a satisfactory idea of its composition can be obtained.

CHEMISTRY AND PHARMACY OF VEGETABLE DRUGS

PART XIV.—ALKALOIDAL DRUGS. 8, Opium

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IN one of his dissertations on medicine, Thomas Sydenham, the great seventeenth century physician and founder of modern clinical medicine, remarked that "without opium I would not care to practise medicine." This observation would doubtless be endorsed by most physicians of to-day. Opium, when considered in association with the use of its isolated alkaloids, is probably the most important drug known to mankind.

The drug consists of the dried latex obtained from the unripe capsule, or fruit, of *papaver somniferum*, a species of poppy bearing white or bluish-purple flowers. The capsule of this plant is usually one or two inches in diameter and therefore much larger than that of the European red poppy. Opium is produced commercially in Asia Minor, European Turkey, Persia, India, and China. The mode of production and appearance of the drug varies with the country of origin. Most of that used for medicinal purposes in this country comes from Asia Minor and Persia, and only the material from these countries will be considered here.

Production of Turkey Opium.

The opium poppy requires a moist soil and careful attention, and in Asia Minor is mostly cultivated by peasant proprietors. The seed is usually sown in December and after the fall of the flowers in June the plants are ready for incision, which is accomplished by cutting each capsule transversely so that the juice slowly exudes during the night. In the morning the partially dried latex is transferred to poppy leaves and allowed to dry further for a few days in a shady place. It is then sold to dealers who make it into large cakes, wrap it in poppy leaves, cover

each cake with rumex fruit, and pack them into bags. Rumex fruit consists of discs about the size of confetti and is used to prevent the cakes of opium from sticking together.

Classification.

The consignments are sent to Smyrna and there opened in the presence of a public examiner, who classifies each cake into "prime," "current" and "chiquiti," according to the appearance. "Prime" opium is supposed to contain a comparatively small amount of matter insoluble in water and is mainly exported to South America for the preparation of smoking opium; in the English market it is termed "shipping" quality. "Current" opium is selected for its value in the preparation of medicines and is the ordinary Turkey opium of our home market where it is designated "druggist's" quality. "Chiquiti," known here as "manufacturers'" opium, is inferior to the other grades and is largely used for the preparation of morphine.

Appearance of Turkey Opium.

The "druggist's" quality consists of cakes or balls varying from about one half to two pounds in weight, and contains a considerable proportion of broken poppy capsules. Each piece is covered with dried poppy leaves and discs of rumex fruit. It is shipped in metal-lined cases holding about 160 lb. Its consistency approximates to that of cheese but varies with the moisture content. The colour varies from light brown to nearly black, while the odour is decided and characteristic.

Production of Persian Opium.

The cultivation centres round Ispahan

Table I.—THE PRINCIPAL PREPARATIONS CONTAINING OPIUM.

NAME.	PER CENT. MORPHINE.	SOLVENT OR DILUENT.	MAIN CONSTITUENTS OTHER THAN OPIUM.	REMARKS.
Powdered opium ..	10	Lactose	—	Used for official mixed powders and suppositories.
Tincture of opium ..	1	Alcohol (about 45 per cent.).	—	—
Camphorated tincture of opium.	0.05	Alcohol (about 56 per cent.).	Camphor, benzoic acid, oil of anise.	Called paregoric.
Suppository of lead with opium.	$\frac{1}{16}$ grain in each	Oil of theobroma .	Lead acetate ..	Used for hæmorrhoids.
Dry extract of opium	20	Calcium phosphate	—	Used for pills.
Aromatic powder of chalk with opium.	0.25	Sucrose	Chalk, cinnamon, nutmeg, clove, cardamom.	Prescribed for treatment of diarrhœa.
Powder of ipecacuanha and opium.	1	Lactose or potassium sulphate.	Ipecacuanha ..	Diaphoretic for colds, etc. Called Dover's powder.
Compound powder of kino.	0.5	—	Kino, cinnamon..	Remedy for diarrhœa.
Compound powder of opium.	1	—	Black pepper, ginger, caraway.	—
Liquid extract of opium.	0.75	Alcohol (about 18 per cent.).	—	—
Ammoniated tincture of opium.	0.1	Alcohol (about 70 per cent.).	Ammonia, benzoic acid, oil of anise.	—
Compound pill of soap	About 2	Corn syrup ..	Hard soap ..	—
Pill of lead with opium	About 1.2	Corn syrup ..	Lead acetate ..	Remedy for diarrhœa
Pill of ipecacuanha with squill.	About 0.5	Corn syrup ..	Ipecacuanha, squill, ammoniacum.	—
Tincture of opium with saffron.	About 0.5	Detannated sherry	Saffron, cinnamon, cloves.	Called Sydenham's laudanum.
Opium lozenges ..	$\frac{1}{16}$ grain in each.	Sucrose, acacia, tolu.	—	For coughs.
Vinegar of opium ..	About 1	5 per cent. solution of acetic acid.	Nutmeg, sucrose.	—
Sedative solution of opium.	1	Dilute alcohol and sherry.	—	Used in place of the tincture.
Opium wine	About 1	Detannated sherry	Cinnamon, cloves.	Gastro-intestinal sedative.
Gall and opium ointment.	0.75	Benzoinated lard.	Gall	—

Contrary to the practice of other countries pale-coloured material is the most esteemed; consequently the capsules are cut during the evening and the inspissated juice is collected just before sunrise, since daylight rapidly discolours the exuded latex. In order to exclude the light of advancing day, the masses of drying juice are conveyed from the plantations in copper vessels instead of on poppy leaves. The juice is dried in sheds until its weight is reduced by about one-fifth, and then mixed with 20 per cent. or more of sarcocolla gum, or else with grape juice, the product gently boiled with constant stirring, and the resulting paste moulded into bricks, each of which is wrapped in red paper. It is shipped from Bushire or Bundar Abbas.

Appearance of Persian Opium.

The material has a homogeneous texture and resembles chocolate in appearance, although it does not crumble when cut with a knife. It is harder and more constant in quality than the opium of other countries, although generally the proportion of physiologically active constituents is not quite so high.

Chemistry of Opium.

Twenty-five alkaloids have been isolated from opium. Of these, morphine ($C_{17}H_{19}O_3N$) is the most important and generally occurs to the extent of 10 to 13 per cent. in "druggist's" quality Turkey opium, while 9 to 11 per cent. is usually contained in the Persian drug. Codeine, which is morphine methyl ether ($C_{18}H_{21}O_3N$), ranks second in importance to morphine and is present to the extent of 0.3 to 1.9 per cent. With the possible exception of papaverine, the other alkaloids of opium are not of medicinal importance, although salts of narcotine, narceine, and thebaine are very occasionally used. For the most part the alkaloids occur in the drug combined as salts with meconic and sulphuric acids. Other constituents include mucilage, sugar, wax, and salts of calcium, magnesium, and potassium.

Therapeutic Uses of Opium.

The physiological action of opium is essentially hypnotic and is mainly due to the morphine which it contains. Most of the alkaloids present have similar, though not identical, therapeutic properties but

are not present in sufficient quantity to render the action of opium widely different from that of its principal constituent. The drug depresses the sensory nerve cells in the cerebrum without affecting the motor nerves. The sedative action first diminishes the normal self-control and, in small doses, results in an apparent stimulation consequent on the removal of the restraint which ordinarily governs behaviour. In larger doses sensations of pain are eradicated and it is the best drug known for the treatment of sleeplessness due to painful disease; for this purpose salts of morphine itself are usually employed.

Apart from its narcotic action opium augments the secretion of perspiration by dilating the skin vessels and thus affords a remedy for catarrhal disorders. In respiratory diseases opium, morphine or codeine are used to check cough and dyspnoea; for this purpose it is often combined with expectorants such as *ipecacuanha*.

Pharmacy of Opium.

The number of preparations containing opium is so large that space will not allow of their individual description, and only the more important galenicals will be discussed. In Table I. the general character of a large number of opium preparations is indicated.

Tincture of Opium, or Laudanum.

This is standardised to contain 1 per cent. of anhydrous morphine, and is prepared by adding boiling water to the sliced drug, setting aside for six hours, adding an equal volume of 90 per cent. alcohol and, after allowing the mixture to stand for 24 hours, straining and pressing the marc. After mixing the liquids the preparation is kept for 24 hours, filtered, and assayed for its morphine content. The strength of the tincture is then finally adjusted by adding a mixture of equal volumes of 90 per cent. alcohol and distilled water. The tincture is specially used in preference to solutions of morphine to allay gastric and abdominal pain in diarrhoea and dysentery, and wherever delayed absorption is desirable.

Paregoric.

This preparation, also known as compound tincture of camphor or camphorated tincture of opium, is prepared by diluting

5 vols. of tincture of opium to 100 vols. with a solution of benzoic acid, camphor and oil of anise in 60 per cent. alcohol. The finished product contains 0.05 per cent. of morphine and 0.3 per cent. of camphor. It is extensively used in the treatment of cough.

Dry Extract of Opium.

The dry extract is mainly employed in the preparation of pills. It is prepared by treating the sliced opium with boiling water and, after 6 hours, straining and pressing the marc. The liquids are mixed and the product assayed for total solids and for morphine content. The preparation is then evaporated to dryness after adding the necessary amount of calcium phosphate to produce a dry extract containing 20 per cent. of morphine.

Dover's Powder.

Frequently termed compound powder of ipecacuanha, this preparation contains 10 per cent. of opium, together with ipecacuanha and lactose. Thomas Dover, the originator of this valuable diaphoretic, was at one time a buccaneer and in 1709, as captain of the privateer *Duke*, rescued Alexander Selkirk, who had lived alone on an island for over four years. Returning with his ship full of treasure in 1710, Dover set up in medical practice with no other qualification apart from having once been a servant of Dr. Thomas Sydenham.

Assay of Opium.

Opium is almost invariably evaluated on its content of morphine and a very large number of processes for effecting this have been proposed. Morphine, although responding to most of the tests characteristic of alkaloids, differs from the majority of these bodies in being almost insoluble in chloroform, ether, or petroleum spirit. The methods of morphinometric assay do not follow on the same lines as the processes for assay generally adopted for other alkaloidal drugs. The following method involves the principle most usually favoured in this country :—

Eight gm. of a carefully prepared representative sample of the batch under test is triturated in a mortar with 2 gm. of calcium hydroxide and 20 ml. of water until a uniform mixture results, when an additional 60 ml. of water is added and the mixture stirred occasionally during half

an hour. The mixture is filtered through a pleated paper and 51 ml. of the clear filtrate, containing the morphine as water-soluble calcium morphinate, is transferred to a flask and mixed with 5 ml. of 90 per cent. alcohol, 25 ml. of ether, and 2 gm. of ammonium chloride. The ammonium salt reacts with the calcium morphinate liberating the morphine alkaloid which settles out as a precipitate, the ether dissolving all other alkaloidal material. After vigorous shaking during half an hour the flask is set aside overnight, the morphine collected in a Gooch crucible and the flask and precipitate washed repeatedly with morphinated water (a saturated solution of morphine in water containing 0.25 per cent. by volume of chloroform). The crucible is transferred to a beaker containing 20 ml. of decinormal sulphuric acid and about 100 ml. of water, the liquid is boiled for a few minutes until all the morphine has dissolved and, after allowing to cool, the excess of acid is titrated with decinormal sodium hydroxide using methyl red as indicator. Each ml. of decinormal acid is equivalent to 0.02852 gm. of morphine. To the amount indicated by the titration 0.051 gm. is added to correct for the loss of morphine due to its solubility.

Assay of Tincture of Opium.

Forty ml. of the sample is evaporated until its volume is reduced to about 10 ml., 1 gm. of calcium hydroxide is added and, after mixing, the liquid is diluted to 41 ml. with water. After half an hour the mixture is filtered, 25 ml. of the filtrate is transferred to a flask and treated with 2.5 ml. of 90 per cent. alcohol, 15 ml. of ether and 1 gm. of ammonium chloride. The process is then the same as for the assay of opium itself excepting that 0.025 gm. is added to the result to compensate for the loss of morphine due to its solubility.

Isolation of Morphine.

On a manufacturing scale morphine may be isolated by triturating opium with sufficient calcium chloride solution to form a thin paste, and extracting with hot water. This converts the morphine and other alkaloids into their respective hydrochlorides, while the acids with which they were combined in the drug are precipitated as insoluble calcium meconate and calcium sulphate. The insoluble

Table II.—THE PRINCIPAL PREPARATIONS OF MORPHINE AND ITS DERIVATIVES.

NAME.	Per cent. Morphine Hydrochloride	Per cent. Codeine.	Per cent. Diamorphine Hydrochloride	Per cent. Apomorphine Hydrochloride.	OTHER CONSTITUENTS.	REMARKS.
Tincture of chloroform and morphine, B.P., 1885.	0.2	—	—	—	Chloroform, ether, etc. (see text).	A favoured form of chlorodyne.
Injection of morphine	2.5	—	—	—	Sterile water ..	Administered subcutaneously. Dose 3-10 minims.
Bismuth and morphine insufflation.	0.4	—	—	—	Bismuth subnitrate, powdered acacia.	Ferrier's snuff for nasal disorders.
Solution of morphine hydrochloride.	1	—	—	—	Hydrochloric acid 0.2 per cent., dilute alcohol.	—
Compound chloroform mixture.	0.09	—	—	—	Hydrobromic acid, chloroform, cherry-laurel water, syrup.	—
Morphine suppository	$\frac{1}{4}$ grain in each	—	—	—	Oil of theobroma.	—
Compound tincture of chloroform and morphine.	0.229	—	—	—	Chloroform, ether, hydrocyanic acid, liquorice, peppermint, etc.	A form of chlorodyne.
Chlorodyne lozenge. .	$\frac{1}{10}$ grain in each	—	—	—	Chloroform, ether, peppermint, capsicum, sucrose, etc.	Valuable for coughs
Morphine lozenge ..	$\frac{1}{30}$ grain in each.	—	—	—	Sucrose, acacia, tolu.	—
Morphine and ipécacuanha lozenge.	$\frac{1}{30}$ grain in each.	—	—	—	Ipecacuanha, sucrose, acacia, tolu.	—
Solution of morphine acetate.	1 (acetate)	—	—	—	Sucrose, acacia, tolu.	—
Solution of morphine tartrate	1 (tartrate)	—	—	—	Dilute alcohol ..	Used for injection.
Codeine jelly ..	—	0.2	—	—	Citric acid, glycerin, gelatin, etc.	Codeine does not induce drug habit.
Compound tablets of acetanilide with codeine.	—	$\frac{1}{4}$ grain in each.	—	—	Acetanilide, caffeine, sodium bicarbonate.	A strong sedative.
Linctus of codeine ..	—	0.25 (phosphate).	—	—	Citric acid, chloroform, quillaia, tragacanth.	For coughs and throat disorders.
Syrup of codeine phosphate.	—	0.5 (phosphate).	—	—	Syrup	Used for making linctus of codeine.

Table II.—Continued.

NAME.	Per cent. Morphine Hydrochloride.	Per cent. Codeine.	Per cent. Diamorphine Hydrochloride.	Per cent. Apomorphine Hydrochloride.	OTHER CONSTITUENTS.	REMARKS.
Compound elixir of diamorphine and pine.	—	—	0.05	—	Oil of pumilio pine, terpin, hydrate, sucrose, etc.	Remedy for coughs and bronchial affections.
Elixir of diamorphine and terpin with apomorphine.	—	—	0.046	0.057	Terpin hydrate, glycerin, syrup of wild cherry, etc.	Do.
Linctus of diamorphine.	—	—	0.1	—	Hyoscyamus, chloroform, tolu, syrup of wild cherry, etc.	Do.
Camphorated linctus of diamorphine.	—	—	0.046	—	Camphor, benzoic acid, ipecacuanha, squill, etc.	Do.
Linctus of diamorphine with ipecacuanha.	—	—	0.046	—	Ipecacuanha, hyoscyamus, chloroform, syrup of wild cherry, etc.	Antispasmodic and expectorant.
Linctus of diamorphine and squill.	—	—	0.046	—	Squill, sodium antimonyl tartrate, senega, etc.	Antispasmodic
Linctus of diamorphine and thyme.	—	—	0.046	0.057	Liquid extract of thyme, tolu, glycerin.	Useful for whooping cough.
Compound diamorphine and pine pastilles.	—	—	1/4 grain in each.	—	Oil of pumilio pine, terpin hydrate, gelatin, glycerin.	—
Syrup of apomorphine	—	—	—	0.05	Hydrochloric acid, alcohol, syrup.	Used as an expectorant.

matter is separated by filtration, and, to prevent oxidation, sodium sulphite is added to the filtrate, which is then concentrated *in vacuo* to the consistency of a thin syrup. Sodium acetate solution is added in order to precipitate narcotine and papaverine which are removed by filtration. A small proportion of alcohol is added to the filtrate, the morphine is precipitated by the addition of lime in the presence of ammonium chloride, and, after allowing to stand for some time, the morphine is filtered off. Codeine may be extracted from the filtrate by shaking with benzene.

The crude morphine is washed with benzene to remove traces of codeine then

mixed with boiling water and neutralised with hydrochloric acid, atmospheric oxidation being prevented by covering with a layer of petroleum. Morphine hydrochloride crystallises out on cooling and is purified by recrystallisation from water. If desired, the base may be obtained by precipitating an aqueous solution of the salt with ammonia.

Properties of Morphine and its Salts.

Pure morphine occurs in odourless white needle-shaped crystals, or as a white crystalline powder almost insoluble in water and common organic solvents. The hydrochloride is the most important salt and when pure appears as colourless glistening

needles or as a crystalline powder soluble in water.

Tests for Morphine.

A simple test consists in adding a drop of nitric acid to solid morphine or one of its salts, when an orange-red colour is produced. Another reaction which is very sensitive depends on its property of reducing ferricyanide to ferrocyanide. The test is conducted by adding to the liquid containing a trace of morphine a dilute and freshly prepared solution of potassium ferricyanide (free from ferrocyanide) to which a little ferric chloride has been added; the presence of morphine is revealed by the development of a bluish-green colour.

Another useful reaction for morphine is conducted by adding a small crystal of sodium nitrite to an acid solution of the alkaloid followed by an excess of ammonia, when a brownish-yellow colour is produced. This test may be used for the colorimetric determination of morphine and is employed in the official process for the assay of camphorated tincture of opium. Codeine does not give the reaction, and morphine, present as impurity in salts of codeine, may be detected and determined by this method.

Synthetic Derivatives of Morphine.

Apomorphine ($C_{17}H_{17}O_2N$) is derived from morphine by the abstraction of the elements of water. The hydrochloride is used as a powerful emetic.

Diamorphine, diacetylmorphine, or heroin, is formed by the action of acetic anhydride on morphine. Its physiological action resembles that of morphine but its narcotic effect is weaker. It is particularly useful for allaying irritant coughs due to asthma and bronchitis.

Many other synthetic derivatives of morphine are in use for which various special advantages are claimed. In general, however, their therapeutic effects are similar to those of morphine and they do not call for special comment.

Pharmacy of the Isolated Alkaloids.

A large number of galenicals containing the isolated alkaloids of opium or their synthetic derivatives are in use and the main characteristics of the more important of these are summarised in Table II.

Chlorodyne.

A notable preparation which owes its action mainly to the morphine it contains is chlorodyne. Several formulæ for this have been proposed, one of which consists in mixing together 6 parts of chloroform, 3 parts of tincture of Indian hemp, 1.5 parts of tincture of capsicum, 22 parts of glycerin, 1 part of spirit of peppermint, with 12.5 parts of alcohol; 0.5 part of morphine hydrochloride is dissolved in this liquid and 12 parts of liquid extract of liquorice, 12 parts of mucilage of gum acacia and 25 parts of treacle are added, and the whole made up to 100 parts with more alcohol. The British Pharmacopœia of 1885 included a tincture of chloroform and morphine which is still considered by many physicians to be the best available form of chlorodyne. It consists of chloroform, 12.5; ether, 3.125; alcohol, 12.5; morphine hydrochloride, 0.2; diluted hydrocyanic acid, 6.25; oil of peppermint, 0.1; liquid extract of liquorice, 12.5; treacle, 12.5; and syrup sufficient to produce 100. Both preparations are effective remedies for diarrhœa, colic, flatulence, and coughs.

Drug Habit and Opium.

The administration of opium, by virtue of the morphine which it contains, is liable to lead to a craving for the drug. For this reason the sale and distribution of opium and morphine, with some of its artificial derivatives, is controlled by the Regulations made under the Dangerous Drugs Acts.

An extraordinary immunity to the drug results after long indulgence, so that large quantities are taken in order to satisfy the subject. Thomas De Quincey consumed 9 fluid ounces of the tincture per day before he finally conquered the habit. De Quincey's description of the sensations which precede the sleep due to a dose of opium will form an appropriate conclusion to this account of the most remarkable vegetable drug known to man. "Here were the hopes which blossom in the paths of life, reconciled with the peace which is in the grave; motion of the intellect as unwearied as the heavens, yet for all anxieties a halcyon calm; tranquillity that seemed no product of inertia, but as if resulting from mighty and equal antagonisms; infinite activities, infinite repose."

SOLVENT EXTRACTION METHODS

AS APPLIED IN THE REFINING OF PETROLEUM PRODUCTS

By F. N. HARRAP, M.Sc.

The Edeleanu Process.

THE oldest and probably best-known solvent extraction method in use in the petroleum industry is the Edeleanu process. Originally patented in Great Britain in 1908, this method consists in brief of agitating a petroleum product with liquid sulphur dioxide in quantity comparable with the quantity of the product to be extracted.

The process was originally adapted to the refining of kerosene distillates, particularly those which, when acid refined, proved to burn with smoky flames in wick-fed lamps.

The success of the Edeleanu process in these cases is due to the fact that sulphur dioxide dissolves aromatic hydrocarbons preferentially, from mixtures of aromatic, naphthenic and paraffin hydrocarbons. As would be expected, sulphur bodies, such as mercaptans, which commonly occur in kerosene distillates are also preferentially dissolved by the reagent.

The Original Process.

As originally carried out, the process consisted in mixing together in closed vessels at a temperature of approximately 14° F. (the boiling point of sulphur dioxide) approximately equal volumes of unrefined kerosene and liquid sulphur dioxide. Paddle agitation was used, and after quite a short period of mixing the mixture was allowed to settle and the extract drawn off from the bottom of the washer. This separation presents no difficulty if a sight glass is provided on the agitator, since separation into two distinct layers generally occurs with all normal stocks if more than 25 per cent. of reagent is used under these conditions.

The Raffinate.

The extract and refined stock (generally referred to as the raffinate) are then

conducted to separate steam-heated vessels in which the sulphur dioxide is distilled off and recovered for further use.

The Modern Process—a Continuous Method.

The process is nowadays carried out by a continuous method. The stock is first completely freed from water, after which it is pumped to a vacuum degasifier, and thence into a gas-tight mixer through a precooling bank. The mixer is generally a cylindrical vessel approximately ten times as long as it is wide, set up with its axis vertical.

The precooled stock enters the mixer near the bottom and the reagent near the top. Owing to the differences in specific gravity, the reagent flows down through the stock and in its passage removes the aromatic and other soluble compounds from the stock. Extract is thus able to be drawn off continuously from the bottom of the mixer, while the raffinate is drawn off from the top.

In the continuous process the extraction is generally carried out at a temperature of 10° F. to 15° F. and separation cannot be effected with a lower ratio of solvent to stock than 1 to 10, since the stock dissolves this quantity of reagent without separation at this temperature.

The removal of reagent from raffinate and extract is carried out by steaming as in the bath process previously described.

Aromatic Content and Sulphur Content.

The aromatic content and sulphur content of the raffinate depend on the ratio of solvent to stock used in the extraction, a higher solvent ratio naturally giving a raffinate of lower aromatic and sulphur content. Treatments of from 50 per cent. to 200 per cent. by volume of reagent are frequently given, the latter high ratio treatment being used in the preparation

of such products as railway signal lamp oil, required to be of exceptionally high quality. Very little finishing treatment is required after sulphur dioxide treatment. Some refiners give a slight acid treatment, followed by a soda wash or lime water wash, whilst others give only a soda wash, or a soda wash followed by percolation through roasted bauxite. This last treatment results in a bright sparkling oil of very good colour.

As has been indicated above, kerosenes refined by sulphur dioxide are reasonably aromatic-free and are of lower specific gravity and sulphur content than the parent stocks.

Burning Quality.

Burning quality, as indicated by the quantity of char formed and the filming of glasses, when used in wick-fed lamps, is also considerably improved. A much greater improvement can be effected on a stock containing a low proportion of naphthenes, than on one with a high naphthene content, since paraffins are on the whole of better burning quality than naphthenes, and the latter are not removed to any great extent by the process.

The extract constitutes a valuable source of anti-knock material for addition to both motor spirit and vaporising oil, due to its aromatic nature, and consequent high anti-knock value.

When it is to be used for these purposes, the extract is generally "topped" to 200° C. end point, and the distillate is refined with sulphuric acid. The acid treated spirit is then finished with either caustic soda solution or lime water.

Finished Blend Stock.

The finished blend stock thus produced is much less volatile than normal motor spirit, being really a cut boiling from approximately 150° C. to 200° C. It is therefore blended with a base stock much more volatile than normal motor spirit, the volatility of the base being adjusted generally by the addition of casinghead gasoline, so that the finished blend is of normal volatility. Many of the extracts produced commercially are practically equivalent to motor benzole in blending value, when considered purely from the anti-knock standpoint.

Vaporising oils are generally produced by blending into kerosene a middle cut

from the extract, boiling from 200° C. to 260° C., which has been refined as indicated above.

Modern Extraction Methods for Lubricating Oils.

During the last few years, a demand has been steadily growing for lubricating oils of equivalent quality to the Pennsylvanian oils, which have always been considered to be the best obtainable motor lubricating oils, because of their marked stability to oxidation and their relatively small change of viscosity with change of temperature. These qualities are attributed to the paraffinic nature of the Pennsylvanian oils.

Solvent refining of lubricating oils may therefore be said to have as its main aim, the production of improved oils, as indicated by better viscosity index and stability to oxidation.

Viscosity Measurements.

Since measurements of viscosity are more easily made than those of stability, refiners tended to assess the improvements made by different refining methods on any particular lubricating oil stock by the viscosity slopes of the oils so obtained, i.e., the rates of change of viscosity with temperature. This is very sound practice if applied to the oils obtained from one stock, for it can be assumed that under these conditions of comparison, the flatter the viscosity slope of an oil, the greater is the stability to oxidation. It does not follow, however, that two oils produced from totally different stocks, but of the same viscosity at a given temperature, and the same viscosity slope, will be equally resistant to oxidation.

Dean and Davis's Viscosity Index.

No simple numerical method of expressing the viscosity slope of an oil was available or generally accepted, until the viscosity index of Dean and Davis was proposed. These authors evolved a formula expressing in units the viscosity slopes of oils in terms of a Pennsylvanian oil of low slope, taken as 100, and a Gulf Coast oil of steep slope, taken as 0. Thus it is possible to express in a convenient form, by means of a number, the viscosity index of any oil, from a knowledge of the viscosity at two temperatures, and the formula of Dean and Davis.

Chemical Constitution of Lubricating Oils.

The chemical constitution of lubricating oils is a subject on which very little data are available, because of the complex nature of these oils. By treating an oil with a suitable solvent, the naphthenes and aromatics are preferentially extracted by the solvent, leaving a raffinate paraffinic in nature. This raffinate is of lower specific gravity and higher viscosity index than the original stock, greater differences being obtained as the volume of solvent is increased.

Solvents.

Numerous solvents have been tried, these varying considerably in their selectivity (or in more simple terms, the amount of raffinate which can be produced from any stock, and the paraffinic quality of this raffinate).

Among the most selective of these solvents are benzonitrile, nitrobenzene, benzaldehyde, o-nitrotoluene, dichlorethyl ether, pyridine, furfural, phenol, sulphur dioxide/benzole and sulphur dioxide itself.

Only a few of these have as yet been applied commercially but there is every reason to believe that the processes have been commercially successful.

How Oil is Treated with Solvent.

In carrying out the process, the oil to be treated is agitated, either batchwise or in a counter current treatment plant, with the desired solvent in ratios from 1 to 5 parts of solvent to 1 part of oil. The temperature of treatment is usually chosen so as to be 35° F. to 45° F. below the temperature of complete miscibility of the solvent and oil, when mixed in the proportion used in the plant. In many cases this entails the use of steam-heated vessels, a fact which will be obvious when it is considered that, for instance, aniline and lubricating oil are not completely miscible below 50° C. in the case of fairly naphthenic oils, and that the temperature of complete miscibility increases as the naphthene content is reduced.

Finishing Treatment.

The raffinate from the plant almost invariably contains some of the solvent, which in the case of high boiling solvents such as pyridine, nitrobenzene and phenol must be removed from the oil by vacuum or steam distillation. A chemical treat-

ment to follow the solvent treatment is often considered to be beneficial, in which cases a treatment with a small percentage of sulphuric acid is given, followed by agitation of the tar-free oil with activated earth. A final filtration is then required to free the oil from suspended earth. Some plant manufacturers recommend treatment with decolorising earth at high temperatures up to 600° F. as the only finishing treatment required.

Dewaxing.

The removal of large percentages of naphthenic material from oils by solvent treatment generally causes the cloud points of these oils to rise to values considerably in excess of the cloud points of the stocks processed, especially in the cases of stocks of high wax content. In these cases dewaxing is generally carried out after the solvent treatment.

Extraction with Two Solvents.

A process in which at least one British company is showing interest is the "Duosol" process.

In this process, two solvents are used instead of the more normal one solvent. These solvents are immiscible, one being selective for the paraffinic constituents while the other is selective for the naphthenes. The operation of this process is somewhat analogous to that of fractional distillation, except that the separation is carried out in the liquid phase.

Two solvents which have been successfully used in conjunction are cresylic acid and propane. The propane is the solvent for the paraffin constituents and the cresylic acid for the naphthenes.

How the Process Operates.

In the operation of the process, the charging stock is fed into the centre of the plant, and the two solvents are fed in from opposite directions so that the solutions of paraffins and naphthenes in their respective solvents pass through the system counter currently to each other. Thus the paraffin solvent stream is continually stripping the last traces of paraffinic material from the naphthenic solvent stream and vice versa. The advantage of this process is that crude residuums can be directly handled, even if the asphalt content of the residuum chosen is high,

as the asphalt is removed with the naphthenic bodies. The process can generally be carried out at atmospheric temperature. It is also claimed that with the crudes so far processed, the yield of high grade lubricants produced is the maximum possible from existing processes. The solvent treated oils can be finished directly by contacting with a decolorising clay, thus eliminating the use of sulphuric acid.

The Advantages of Solvent Extraction Processes.

The general advantages to be gained from any of the solvent treatment processes are as follows :—

Stocks which by the conventional acid refining result in poor oils of low stability and viscosity index, can be solvent treated to give high yields of very stable oils of high viscosity index, comparable with the Pennsylvanian oils which the processes were designed to imitate.

Acid Tar.

In processes for the preparation of lubricating oils, in which sulphuric acid is used, large amounts of acid tar are

formed. This acid tar is difficult to dispose of, since it contains a large proportion of acid. In some cases it is found economical to recover the acid from the tar, but in other cases the tar is neutralised and then burned in the refinery. It is obvious that large losses of oil must necessarily be expected in acid refining.

In solvent refining the extracts produced are fairly viscous oils with moderate to good cold tests, which are quite suitable for blending straight into fuel oils. There is therefore no waste product from solvent refining similar to the acid tar produced from acid refining.

Carbon Residues.

One point on which Pennsylvanian oils are often criticised is the high carbon residues of these oils. Oils produced from naphthenic stocks by solvent treatment, to stabilities and viscosity indices comparable with the Pennsylvanian oils, show carbon residues of a lower order than the latter. This is a distinct advantage, since maximum limits for carbon residues are still included in many lubricating oil specifications.

BLEACHING JUTE AND HEMP

THE natural colour of jute varies from a yellow to a French grey, and although jute is often dyed and manufactured without bleaching, it is occasionally necessary to destroy the greater part of its colour, especially if it is required to be dyed in bright and delicate shades.

When bleaching jute yarn in the form of hanks it is not subjected to a preliminary boil with alkalis but is simply immersed in a solution of bleaching powder at a strength of 1° Tw. for about 2 hours and at a temperature of 100° F. After bleaching, the jute is given a thorough rinse and is finally soured in weak acid. This gives a partial bleach, and if a still greater reduction of colour is required the above operation is repeated.

Chlorine readily acts upon jute, being liable to form a yellow coloured chlorine derivative, so that care must be taken in the treatment. Bleached jute readily loses its light colour and on exposure to

light and air tends to turn brown.

Jute pieces are sometimes bleached in a solution of chemick containing 1 per cent. of available chlorine and made alkaline with soda. After the bleach bath they are soured with dilute hydrochloric acid, washed and dried. They may thus be reduced to a light cream shade and at the same time receive a soft handle and become more lustrous.

Hemp Bleaching.

Hemp is a coarse dark-coloured fibre difficult to bleach and is as a rule rarely given a full bleach. When used for the manufacture of string or rope a light bleach can be effected by boiling the hemp in a 2 per cent. solution of sodium silicate (70° Tw.), boiling in water, and then steeping for 24 hours in a 1 per cent. solution of bleaching powder, being finally soured in dilute hydrochloric acid, washed and dried.

HIGH TEMPERATURE MEASUREMENT IN INDUSTRY

By CHAS. R. DARLING, A.R.C.Sc.I., F.I.C., F.Inst.P.

FIFTY years ago it was seldom attempted to measure the high temperatures employed in metallurgical and chemical processes. Since that time a number of correct methods for measuring high temperatures have been worked out and applied in instruments suited to industrial use. The general name of "pyrometer" is applied to these instruments, which have proved so useful that most furnace processes are now controlled by their aid.

How High Temperatures are Measured.

In an ordinary thermometer temperatures are measured by observing the amount by which the mercury expands, but since mercury boils below a red heat, thermometers cannot be used in furnaces. There are many other physical changes produced by an increase in temperature, however, and it has been found that some of these changes can be applied to the measurement of high temperatures.

Four Types of Pyrometers.

Four chief types of pyrometers are now

in use, each based on a different physical change, and in each case the temperature is determined by measuring the amount of the change. These types are known as

(1) thermoelectric; (2) resistance; (3) total radiation; and (4) optical; and each type has its own special advantages for particular purposes. Before describing them, however, it is necessary to explain how the scale of high temperatures used in marking them has been compiled.

High Temperature Standards.

All temperatures are based upon the difference between those of melting ice and steam

at normal atmospheric pressure, the former being called 0°C . or 32°F . and the latter 100°C . or 212°F . In order to extend these readings to the highest temperatures, thermometers with metal bulbs and containing a gas have been employed to obtain a number of fixed points which can be used in marking pyrometers. A thermometer of this kind is not suited to ordinary purposes owing to the many fittings necessary, and the elaborate precautions that must be taken to ensure

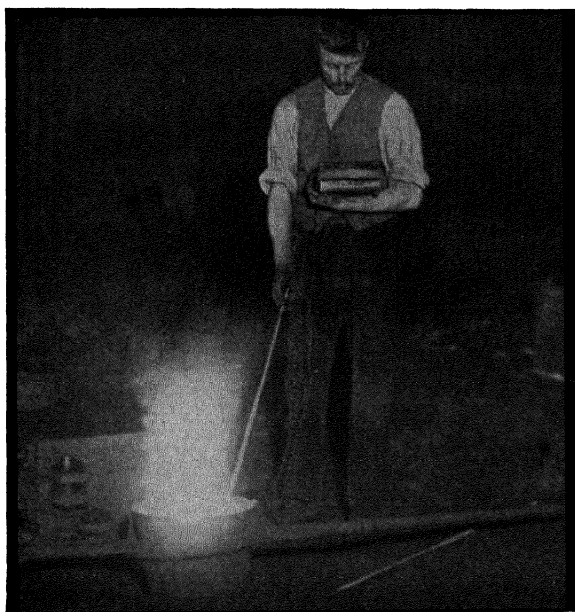


Fig. 1.—A THERMOELECTRIC PYROMETER IN USE FOR DETERMINING THE TEMPERATURE OF A CRUCIBLE OF MOLTEN METAL BEFORE POURING INTO THE MOULDS.

Having inserted the thermocouple, the operator reads the temperature on the indicator when the pointer takes up a steady position.



Fig. 2.—THE CONSTRUCTION OF A THERMOCOUPLE.

In the lower part of the picture the wires are seen threaded through fireclay tubes to keep them apart; they are welded together at the lower end. The free ends are connected to the head as shown and afterwards placed in the sheath. A cable from the head contains the wires which connect to the indicator.

a correct reading. By its aid, however, a number of fixed points have been determined with great accuracy, and are used in the marking of pyrometer scales.

Some of these points are tabulated below :—

Melting point of lead	327° C. or 620° F.
„ „ zinc	419 786
„ „ antimony	630 1,166
„ „ silver	961 1,761
„ „ copper	1,083 1,982

These fixed points can be employed for all pyrometers, so that all types may be made to agree in their readings.

THERMOELECTRIC PYROMETERS.

Principle.

When two dissimilar metals are joined together and the junction is heated, an electromotive force is set up at the junction, and if the free ends of the metals are connected through a galvanometer it will be seen that a current is flowing round the circuit. The E.M.F. changes as the temperature rises, but the nature and amount of this change depend upon the metals used. If a pair of metals can be found which show a steadily increasing E.M.F. as the temperature rises, the scale of a galvanometer to which they are connected may be calibrated so as to read temperatures directly. When thus arranged the pair of metals forms the "thermocouple" and the galvanometer the "indicator."

The Thermocouple.

The metals forming the thermo-

couple must have high melting points, and must be able to stand prolonged heating without changing so as to alter the E.M.F. to which they give rise. The E.M.F. should increase by a minimum of 1 millivolt for 100° C. rise in temperature, in order that the

mechanism of the indicator may be made strong enough to allow portability. Only a few pairs of metals can be found which fulfil all these requirements, and in industrial practice the choice is restricted to two or three couples, according to the temperature to be measured

The Le Chatelier Couple.

For readings up to 1,200° C. or 2,190° F. the Le Chatelier couple is much used, one of the wires being made of pure platinum and the other of an alloy of platinum and rhodium. Owing to the high melting points of these metals this couple can be used to take occasional readings up to 1,400° C. or 2,550° F., but if kept at this temperature for long periods the couple undergoes a permanent change and ceases to give correct readings. The average increase in E.M.F. is a little over 1 mv. per 100° C. rise in temperature, and for work at the highest temperatures named this couple has no superior. The high price of the metals makes it necessary to use them in the form of relatively thin wires, so that the couple has little mechanical strength. The junction is formed by welding the wires together.

Another Type.

Another couple in common use is made up of a thick wire of nickel welded to another composed of an alloy of nickel and chromium, which can be used to measure temperatures up to 1,100° C. or 2,010° F. continuously, and with special precautions to 1,300° C. or 2,370° F. Although inferior in

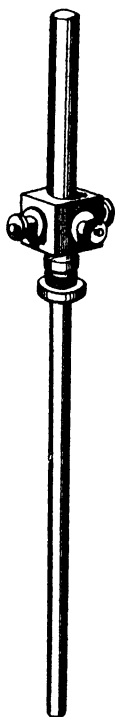


Fig. 3. — A RESISTANCE ELEMENT.

range to the Le Chatelier couple, it has the advantages that its components are cheap, so that thick, strong wires may be used; and that it develops an E.M.F. about four times as large, enabling a more robust indicator to be used. When the readings do not exceed 850°C . or $1,560^{\circ}\text{F}$. a couple of iron and constantan (a nickel-copper alloy) gives good results. Couples formed of the commoner metals are known as "base-metal" couples, in distinction to those made of the rare metals.

Practical Operating Notes.

When used in furnaces in which the atmosphere contains metallic or other corrosive fumes, the couple must be enclosed in an air-tight sheath of refractory material, otherwise it would soon be destroyed. The junction is placed near the closed end of the sheath and the wires are brought to terminals mounted on a head which covers the open end of the sheath. The length is decided by the distance to which it is inserted in the furnace, the junction being located at the spot at which the temperature is to be measured, and the head allowed to protrude several inches outside the furnace.

Inside the head the joints of the wires to the terminals constitute junctions which would affect the readings of the indicator if their temperature should rise, and hence provision against this possibility must be made. This can be done by arranging to keep the head at a constant temperature, or by some device which compensates any error that might arise from this cause. Any maker of pyrometers will provide means of guarding against these "cold-junction" errors.

A typical thermocouple arrangement is shown in Fig. 2.

The Indicator.

Any millivoltmeter of the moving-coil pattern and of the right degree of sensitivity may be used as the indicator. For industrial purposes a pivoted instrument is preferable to one with a suspended coil, being less liable to get out of order. The temperature scale could be prepared by noting the deflection of the pointer when the thermocouple was subjected to a series of standard temperatures, and sub-dividing the intervals. In practice it is easier for the maker to determine the E.M.F. developed by a specimen junction made from his wires at a number of fixed points, and so establish the relation between E.M.F. and temperature.

The indicator can then be marked temporarily in millivolts—an easy

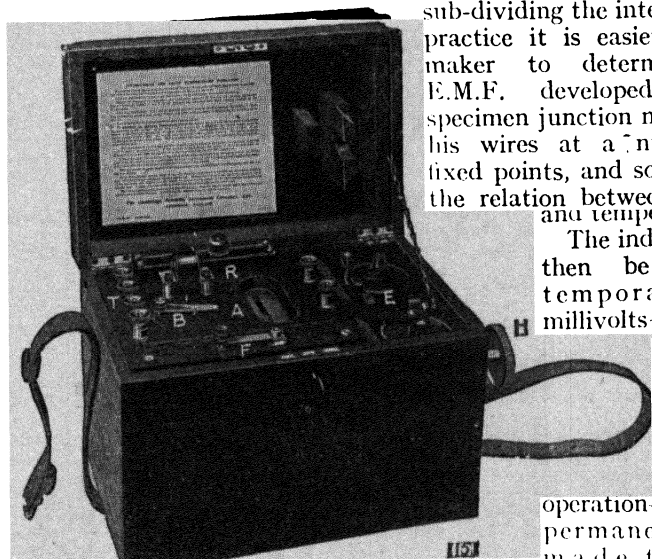


Fig. 4.—AN INDICATOR FOR A RESISTANCE PYROMETER.

The terminals of the resistance element are connected to corresponding terminals at T; the galvanometer is beneath the lid at B, its pointer being visible through a small opening; E is the battery and R is a knob which is turned to adjust the balancing resistance. The temperature is read on a paper scale which moves as the resistance is changed, the figure opposite a fixed mark seen through a window at A gives the temperature in degrees. F is the key for bringing the battery into the circuit.

operation—and a permanent scale made to read corresponding temperatures. In many cases both a millivolt and a temperature scale are marked on the dial. The indicator can be mounted in any suitable position, or can be fixed in a case for transport.

The accuracy of the reading depends upon the size of the scale: at the best a difference of 5°C . can be detected in the working temperature, which is within the range of variation to which industrial furnaces are liable.

Fig. 1 shows a thermoelectric pyrometer in use in a foundry.

RESISTANCE PYROMETERS.

Principle.

All elementary metals show an increase

in electrical resistance when the temperature is raised. A length of platinum wire, for example, having a resistance of 2.6 ohms at 0°C ., increases its resistance to 3.6 ohms at 100°C ., or at the rate of 1 ohm per 100°C .; and copper, nickel and other metals behave similarly. Alloys show a less marked increase, and in some instances are practically unaffected in this respect by temperature. The increase in resistance continues up to the melting point of the metal, so that it is possible to deduce the temperature of a wire from its resistance when the relation between the two is correctly known.

Resistance pyrometers depend upon this principle, and consist of a coil of wire forming the "resistance element" and an indicator which enables the resistance to be measured and corresponding temperatures read.

The Resistance Element.

Platinum is the only feasible metal to use for the resistance element, since it does not oxidise in air, and if shielded from furnace fumes will retain its original properties for a long period. Since the formation of oxide on a wire reduces the diameter of the metal, the resistance at all temperatures will become greater as oxidation proceeds and the diameter of the remaining metal diminishes. No certainty of measurement could therefore be secured by the use of such metals as iron, copper, or nickel; and gold, which does not oxidise, would not cover a sufficient range since it melts at $1,063^{\circ}\text{C}$. or $1,945^{\circ}\text{F}$. Platinum combines the two advantages of resistance to oxidation and high melting point ($1,755^{\circ}\text{C}$. or $3,190^{\circ}\text{F}$.) and is

the metal best suited for the resistance element.

In making the element, a coil of platinum wire is wound round a mica frame in the form of a double spiral, the free ends being connected to leads which pass to terminals fixed on a head composed of insulating material. The resistance of the leads, as well as that of the coil, will change with the temperature, but by placing a pair of dummy leads adjacent to them and exactly similar in size, resistance changes in the proper leads can be compensated. The dummy leads are

brought to a separate pair of terminals on the head, and in the measurement of resistance are opposed to the working leads so that they cancel one another and only the resistance of the coil itself is indicated.

The coil and all the leads are enclosed in a gas-tight sheath to exclude furnace gases, porcelain being generally used. The appearance of a resistance element is shown in Fig. 3.

The Indicator.

The indicator takes the form of a box containing resistance coils, a galvanometer and a battery, arranged to form a Wheatstone bridge. One of the resistances is adjustable, and is used to balance the resistance of the coil, which is connected to the bridge through terminals on the outside of the box, a second pair of terminals being provided for the dummy leads.

How a Reading is Obtained.

To obtain a reading, the adjustable resistance is changed in value until, on pressing a key which brings the battery into the circuit, no deflection is produced

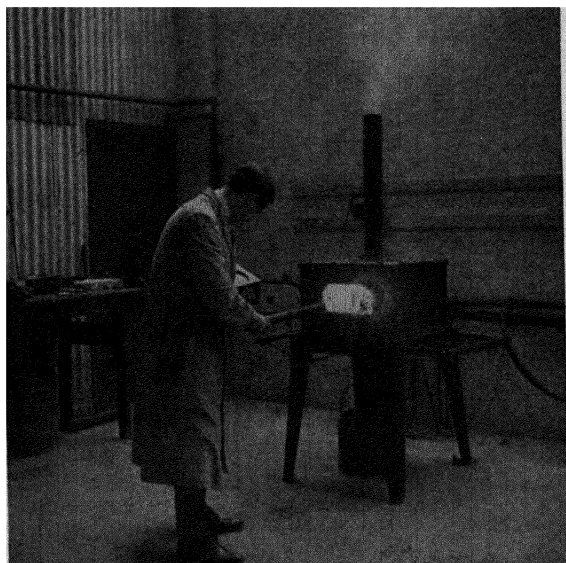


Fig. 5.—A TOTAL RADIATION PYROMETER IN USE
The observer holds the open end of the telescope in front of the furnace and reads the temperature on the indicator, which may be held in the hand or supported otherwise.

on the galvanometer. The resistance of the coil in the furnace is then known, and its temperature can be read on a scale marked in degrees which correspond to different resistances. The change in the resistance of platinum with temperature has been determined with great accuracy, and with a sensitive indicator it is possible to detect a difference of 1° C. at any temperature up to $1,000^{\circ}$ C. Fig. 4 shows an indicator of the type described.

Special Uses of Resistance Pyrometers.

A resistance pyrometer is capable of giving closer readings than other types, and is used when special accuracy is necessary. It is impossible to control the temperature of a large industrial furnace to a closer limit than 5° C., so that advantage cannot be taken of the greater sensitivity of the resistance pyrometer in ordinary working. It has the disadvantage that an adjustment is necessary to obtain a reading, and is more costly than a thermoelectric instrument designed for the same range of temperature; and hence its use is restricted to operations which permit of very exact control of the heat supplied.

In the laboratory it is very useful for research purposes and for testing the accuracy of the pyrometers used in the works. It will give accurate readings over a long period of continuous use at temperatures up to $1,000^{\circ}$ C. or $1,830^{\circ}$ F., and may be used occasionally as high as $1,200^{\circ}$ C. or $2,190^{\circ}$ F., but constant use at the higher temperatures results in a change in the resistance value of the coil and the readings are then discrepant.



Fig. 6.—AN OPTICAL PYROMETER BEING USED TO READ THE TEMPERATURE OF A GAS RETORT.

The telescope is placed opposite a small hole in the door and held in the left hand. The observer turns a knob with his right hand and by doing so alters the resistance of the circuit of the lamp inside the telescope. When the filament disappears, the temperature is read on the indicator in the front.

TOTAL RADIATION PYROMETERS Principle.

An incandescent substance radiates energy in the form of waves, some of which are visible and others invisible. When the radiations fall on a dull black surface they are absorbed, and the energy they possess is converted into sensible heat. The hotter the substance the greater is the amount of energy radiated per second, and a law has been

established which expresses the relation between the temperature of the hot source and the rate at which it radiates energy.

This law states that "the amount of energy radiated in a given time by a full radiator varies as the fourth power of its absolute temperature." Any enclosure at a steady temperature behaves as a full radiator, so that if the energy radiated from a furnace can be measured the temperature can be deduced.

A total radiation pyrometer consists of a receiving tube or telescope which receives the radiations and contains an arrangement for converting the rays which enter it into sensible heat. The relative amounts of sensible heat produced at different temperatures are measured on an indicator, which shows on a scale the corresponding temperatures of the furnace.

The Receiving Tube or Telescope.

Radiations from the hot source are received through the open end of a metal tube, blackened internally and closed at the other end by a concave mirror, which brings the rays to a focus inside the tube. In the focus is placed a small metal disc, blackened on the side facing the mirror so as to absorb the radiations which fall on it.

The temperature of the disc is raised by an amount which depends upon the intensity of the radiations—that is, the temperature of the source of heat—but under no conditions does the temperature of the disc itself exceed 100°C . On the back of the disc two wires of different materials are soldered, and their free ends brought to insulated terminals on the outside of the tube. These wires form a thermocouple which serves to

measure the rise in the temperature of the disc, which is proportional to the amount of radiant energy it receives

When the thermocouple is connected to a galvanometer changes in the temperature of the hot source are shown by movements of the pointer, and by suitably marking the scale the temperature of a furnace may be read from the position of the pointer. In taking a reading, the open end of the telescope must be placed within a given distance from the furnace, specified by the makers, in order to secure a correct result. Beyond this distance, owing to spreading, the radiations received by the telescope will be too small in quantity to heat the disc fully and the readings will be too low.

The Indicator.

This consists of a specially sensitive moving-coil galvanometer, which must give full-scale deflection when the couple on the disc is heated by radiations from the hottest source for which the pyrometer will be used. The galvanometer is connected to the terminals of the thermocouple on the outside of the telescope, and

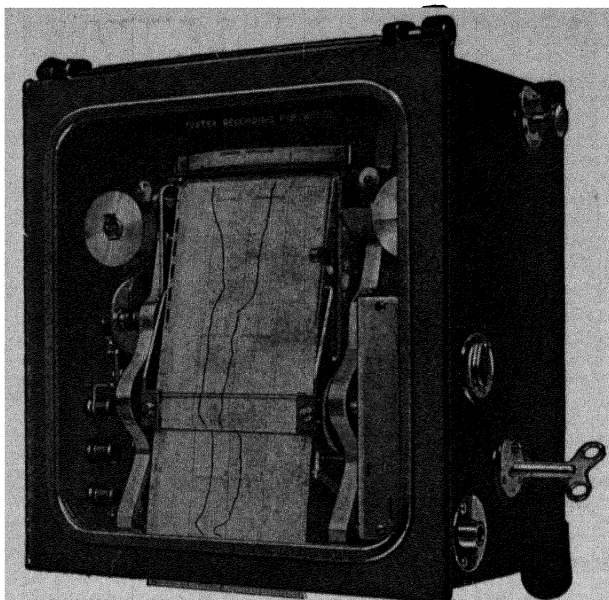


Fig 7.—A RECORDER FOR A THERMOELECTRIC PYROMETER

The curved bar which depresses the pointer of the galvanometer is above the top of the chart. The paper is moved forward by a clock which is wound up by a key at the side. Internal terminals are provided for connecting the thermocouples. The records of two furnaces are shown on the chart.

its ordinary scale indicates the E.M.F. of the couple at the temperature of the disc.

In order to prepare a scale showing furnace temperatures, the telescope is placed in front of a furnace the temperature of which is exactly measured by other means, such as a resistance pyrometer. The position of the pointer can then be marked on a second scale to conform with this temperature, after which the other temperature

markings can be obtained by applying the fourth-power law.

Indicators can be made to cover any desired range of temperature between 700° and $2,250^{\circ}\text{C}$. or $1,290^{\circ}$ and $3,980^{\circ}\text{F}$. by adjusting the size of the entrance aperture of the telescope, and hence can be made to read temperatures at which the best thermocouples would be destroyed.

Fig. 5 shows a radiation pyrometer being used with a gas-fired furnace.

Special Uses of Total Radiation Pyrometers.

The great advantage of this type of pyrometer is that no part is subjected to the temperature of the hot source, so that there is no danger of destroying any of its parts. It can therefore be used to measure the temperature of electric furnaces and other intense sources of heat, and also that of molten substances which would attack the sheath of a thermocouple and penetrate to the wires.

It can be pointed to any part of a furnace, so that the temperature of any particular object can be measured, whereas a fixed thermocouple gives a reading which applies only to the part in which it is



Fig. 8.—A GROUP OF FURNACES FITTED WITH TEMPERATURE ALARMS.

When a green light shows on the front of an alarm, the attendant increases the heat supply; when the red light, shows it is reduced. When neither is seen the furnace is at the correct temperature.

placed. Its portability is a further advantage, enabling it to be used for special purposes at any part of the works. Certain precautions are necessary when using it.

If visible fumes intervene between the hot source and the telescope, some of the radiations will be impeded and the readings will be too low. Whenever possible, readings should be taken while the object is inside the furnace, and the conditions of full radiation are realised.

If a block of steel, for example, be removed from a furnace and the telescope placed in front of it the temperature indicated will be too low, because the surface is an imperfect radiator. When inside the furnace, the block reflects heat from the walls in addition to that which it radiates, and the total amount then leaving the surface is then equal to that of a full radiator, so that its correct temperature is measured. When it is necessary to take a reading outside the furnace a correction must be applied, the nature of which will be stated by the maker in any given case.

OPTICAL PYROMETERS.

Principle.

When a substance becomes visibly hot its brightness increases rapidly as the temperature rises, and this applies not

only to the total amount given out but also to the component colours of the light. The relation between the increase in the brightness of any chosen part of the spectrum and the rise in temperature is accurately known, so that measurements of brightness under proper conditions enable temperatures to be deduced. It is usual to measure the brightness of the red part of the spectrum, as red glass can be made which transmits only this colour and cuts off the remainder, so that if a furnace is viewed through it only the red part of the light is seen. A photometric device is used for the measurement, and the results obtained are translated into temperatures.

The Photometer.

The "disappearing filament" type of photometer is most commonly used in pyrometers and will be described here. It consists of a telescope through which the furnace is viewed, the object glass being movable for the purpose of focusing so as to obtain a sharp image. In front of the eyepiece a piece of red glass is placed, so that the image will always appear red in colour, but of varying brightness according to the temperature.

Inside the telescope is fixed a small electric lamp with a straight filament so that the filament is in the focus of the

eyepiece. This lamp is lighted by a small accumulator through an adjustable resistance, by means of which the brightness of the lamp may be varied, and a milliammeter in the circuit measures the current taken by the lamp.

When taking a reading, the telescope is focused so as to give a sharp image of the hot source, and the brightness of the filament adjusted until it is the same as that of the background formed by the image. When equality is obtained the filament loses its sharp outline, and the matching is very definite, since a change of a few degrees makes the filament stand out either brighter or darker than the background. The reading on the milliammeter is then noted.

The Indicator.

The milliammeter is provided with a scale which enables the temperature of the filament to be read from the amount of current taken, and when correct adjustment has been made the temperature of the furnace will be the same as that of the filament.

This scale is prepared by making a number of observations at known temperatures, the current taken by the filament when matched being noted in each case and marked in corresponding temperatures on the second scale. The intervals between these points are then suitably sub-divided and the scale extended in conformity with the current-temperature relation thus found.

When the lamp at its hottest is less bright than the furnace, a dimming glass is placed in front of the objective of the telescope to reduce the brightness of the entering light, and another temperature scale used which has been prepared with the dimming glass in position. Fig. 6 shows an optical pyrometer in use.

Special Uses of Optical Pyrometers.

There are some instances in which temperatures are required which cannot be measured by other methods, owing either to the temperature being too high or difficulty of access—a stream of molten steel, for example. In such cases an optical pyrometer is the only kind that can be used; but in addition it can be employed for taking occasional readings of furnaces, etc., which are not provided with a fixed pyrometer. Optical pyro-

meters are not intended to read below 800° C. or 1,470° F., but can be used for the highest attainable temperatures. The necessity of making an adjustment, although of a simple kind, when taking a reading is a drawback from the workshop standpoint. As with the total radiation pyrometer, low readings result when visible fumes intervene between the furnace and the telescope, or if the hot object sighted is in the open. In the latter case a correction may be applied according to information supplied by the maker.

RECORDERS.

Much useful information can be gained from a continuous record of the temperature of a furnace, and many firms use automatic recorders, mainly in conjunction with thermoelectric pyrometers.

In these instruments a curved bar is placed over the pointer of the galvanometer and by a mechanical device made to descend at regular intervals and depress the end of the pointer on to a paper chart. The paper is moved forward continuously by clockwork or an electric motor, and is divided so as to read time lengthwise and temperatures horizontally. After a dot has been made, the curved bar rises and frees the pointer, which then takes up the position determined by the temperature of the furnace, after which the curved bar again descends and the procedure is repeated. The dots are so close together as to form a nearly continuous line from which the temperature at any given time can be read off.

To obtain records with a total radiation pyrometer the receiving tube must be fixed opposite a hole in the wall of the furnace and a chart used which has a temperature scale marked so as to agree with the readings on its indicator. Fig. 7 shows a recorder of the type described; two records, taken simultaneously, being shown on the chart.

Recorders are also made for resistance pyrometers in which the pointer of the galvanometer is made to complete relay circuits when it swings a short distance on either side of the central position.

We are indebted to the Foster Instrument Co. and Messrs. A. Gallenkamp & Co., Ltd., for the loan of the illustrations which accompany this article.

ARTIFICIAL SILK

THE VISCOSE PROCESS

By L. HEBBS, A.I.C.,
of Messrs. Cross & Bevan



Fig. 1.—PULP SHEETS BEING CUT TO SIZE AND STACKED.

IN the production of rayon by the viscose process, cellulose is brought into a water dispersible condition, as sodium cellulose xanthate, and is subsequently regenerated as continuous thread.

The reactions leading to this result were discovered and patented in 1892, and the viscous dispersions obtained were then given the name "Viscose." Although now in general use this name is a registered trade mark still held by one of the companies formed to exploit the process, as early as 1894. During the period 1892 to 1904 attempts to produce artificial silk, or, as it is now called, rayon, met with little commercial success, and development was chiefly towards the production of carbon filaments for electric lamps, and sizing materials for textiles and paper. The viscose rayon industry may be said to have really commenced in 1903-4,

when Messrs. Courtaulds and the Société Française de la Viscose entered the field. Since that date there has been continuous growth, which in recent years has been so rapid that the viscose process was responsible for the production of almost eight hundred million pounds of rayon during 1934, which was about 88 per cent. of the total world output.

Raw Materials.

The raw materials required for the production of viscose are cellulose, caustic soda, and carbon disulphide, and of these the cellulose presents the more involved analytical problems, which will briefly be considered.

Since almost all the tests available for the examination of cellulose are empirical, rigorous attention to detail is essential to obtain reproducible results, and it is

not possible to give all the necessary details in the scope of the present article.

Bleached chemical wood pulp, produced by the bisulphite process, is the chief cellulosic raw material for the industry, although a small and diminishing amount of cotton linter pulp is still employed. The wood pulp is received in board form, the sheets averaging between 550 and 650 gm. per square metre, and containing from 6 to 10 per cent. of moisture. This moisture content is estimated in the usual way by drying at 100° to 105° C., and the other analytical values are generally calculated to oven dry basis.

Alpha Cellulose Content.

This fraction is usually defined as the amount of cellulose insoluble in "mercerising soda." The pulp is treated with strong soda solution under standardised conditions, usually 17.8 per cent. weight/weight caustic soda solution for 30 minutes at 20° C. The solution is then diluted and the pulp washed practically free from alkali. Acetic acid is then added, and after further washing the residue is oven dried and weighed.

The Alpha cellulose content should therefore be defined as that fraction which, following mercerisation, is insoluble in caustic soda solutions through the concentration range from 17.8 per cent. down to 0 per cent. This distinction is important, since maximum solubility for wood pulp cellulose occurs at around 9 per cent NaOH concentration.

The Alpha cellulose content should be maintained at a high value since this will affect both the yield and quality of the yarn obtained

Beta Cellulose Content.

The alkaline filtrate from the Alpha cellulose is made acid, and the precipi-

tated Beta cellulose can be filtered off, dried, and weighed.

Low Beta cellulose content is generally indicative of restrained action in the cooking and bleaching processes, during the production of the wood pulp.

Gamma Cellulose Content.

This is the permanently soluble fraction, and may be estimated by difference, or, alternatively, can be determined by oxidising with dichromate.

Although a high Gamma cellulose content will mean loss in yield of yarn obtained, nevertheless a relatively high value is often preferred, since it is frequently found to correspond with desirable reactivity in the pulp.

Copper Number.

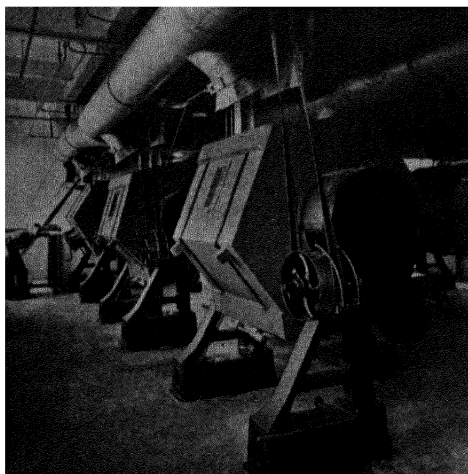
Defined as the number of milligrammes of copper reduced per gramme of cellulose, this value was formerly regarded as an indication of the bleaching treatment given to the pulp. In these days of alkaline bleaching and washing, copper numbers have much less significance.

A number of methods are available, but the one in most general use in this country is the Clibbens and Geake modification of the Braidy method, as published in the Shirley Institute Memoirs, 1923. The physical condition of the pulp affects the results obtained, and the samples should, therefore, be subdivided and screened in standardised fashion.

Mineral Matter.

The ash content is determined in the usual way, but volatile sodium salts are lost if very high temperatures are employed. The total mineral matter present, including sodium salts, may be obtained by moistening the pulp with sulphuric acid and gently burning off as sulphates.

Low ash content is obviously desirable,



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Fig. 2 —ROTATING CHURNS IN WHICH ALKALI CELLULOSE IS CONVERTED TO XANTHATE BY REACTION WITH CARBON DISULPHIDE

in view of the possibility of jet and filtration stoppage, although ash contents are now so low that they are probably only of secondary importance in this connection.

Cuprammonium Viscosity.

The cuprammonium viscosity is usually estimated at 1 per cent. cellulose concentration, using the method recommended by the Fabrics Research Committee of the Department of Scientific and Industrial Research. The results may be reported as centipoises or fluidity (reciprocal poise).

In general it may be stated that the cuprammonium viscosity should be as high as is possible, consistent with a spinnable viscose viscosity.

Swelling Factor.

This characteristic may be determined by treating the pulp with mercerising soda, and determining the increase in weight or volume of the sheet. The swelling factor is usually represented as a ratio between original weight and amount of liquid taken up. A high swelling factor is generally desirable where possible, but a mechanical limit is sometimes imposed by the dimensions of the steeping tanks.

Resin Content.

The ordinary Soxhlet apparatus is generally employed for this determination, but a wide range of solvents and mixed solvents are in vogue. The most general for viscose pulp are ether, ether/alcohol, or acetone. Some workers determine the ash content of the extract obtained, in order to allow for the mineral content derived from resin soaps. Low resin content is obviously desirable, and recent viscose pulps have shown marked improvement in this connection.

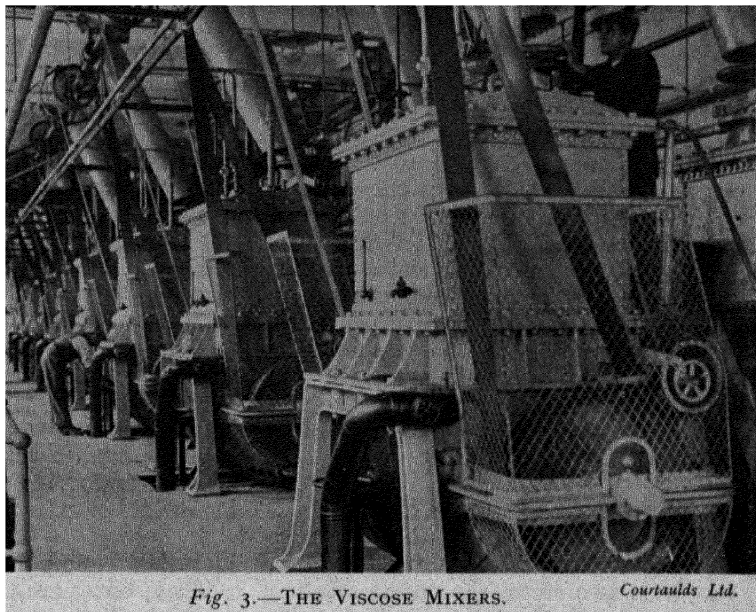


Fig. 3.—THE VISCOSE MIXERS.

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In addition, the lignin content, the wood gum number, the Mahood soda solubility, and similar values, may be of interest for special purposes.

Typical Values for Good Grade Viscose Pulp.

The following may be taken as typical values for modern good grade viscose pulp:—

Alpha cellulose.. .. .	90.6%
Beta cellulose	2.3%
Gamma cellulose (by difference)	7.1%
Copper number (Braid's method)	1.2
Ash	0.09%
Cuprammonium viscosity (1% cellulose,) centipoises ..	24.8
Swelling factor (by weight) ..	6.5
Acetone soluble resin	0.4%

The Manufacturing Process.

The pulp is received at the viscose mill in bales weighing about 2 cwts., in which the sheets measure 36 in. by 26 in. or more. These sheets are cut into either two or four pieces by guillotine, and the pulp is then brought into equilibrium with air at known and controlled relative humidity. This may be accomplished by loose stacking or putting in racks, or more quickly by passing through a tunnel with a counter-current air circulating system.

The Steeping Tanks.

A weighed quantity is then fed to steeping tanks, in which the sheets are stood on edge and separated at regular intervals by perforated iron plates. Caustic soda solution of about 17.8 per cent. concentration is then run into the tanks, but the level of the liquid is only allowed to rise slowly, so as to avoid entrapping air as far as possible, and to obtain even penetration of the pulp sheets. During this steeping the pulp sheets increase in thickness by some 500 to 600 per cent., and it is essential that there should be sufficient clearance to allow free movement during this "swelling." Hence the importance of swelling factor in relation to the press dimensions.

The Pulp Sheets are Now Pressed.

After about two hours the hydraulic ram is slowly moved up along the tank, in at least two steps, the excess solution is run off, and the pulp sheets heavily pressed until they retain only twice their weight of soda solution. The soda solution removed contains some of the Beta and Gamma cellulose fractions extracted from the pulp, and the concentration of these hemicelluloses may rise to 2 to 3 per cent. in the final portion of liquor removed from the pulp.

In some few mills the soda solution is re-used without regard to its hemicellulose content, but the usual practice now is for this solution to be run to the dialysing plant for recovery.

After pressing, the moist sheets are discharged from the press, mechanically or by hand, and weighed to check the ratio of cellulose to liquor left in the alkali cellulose.

Grinding.

The moist sheets are then disintegrated in a jacketed kneading machine, having serrated arms and central blade. About three hours' grinding is necessary to produce the loose, open, crumb-like material required, and during this period a considerable quantity of heat is produced mechanically, in addition to that arising from the oxidation of the alkali cellulose, which is proceeding simultaneously with the grinding. The circulation of cooled brine in the outer jacket is intended to prevent local overheating at the grinding surfaces, but the temperature of the crumbs as a

whole is generally allowed to rise by a fixed amount (about 5° C.), during the disintegration.

Examination of Alkali Cellulose Crumbs.

The alkali cellulose crumbs are generally examined for cellulose and soda content, and in addition the apparent specific gravity may also be determined, and the following may be taken as typical values:

Alpha cellulose	27-28%
Caustic soda	14.5-15.5%
Sodium carbonate	0.5-0.8%
Weight per litre	250-300 gm.

The kneading machine is so constructed that the trough can be raised into a horizontal position, whilst the blades are still rotating, and in this way the crumbs are transferred to a number of small rectangular metal boxes.

Maturing Period.

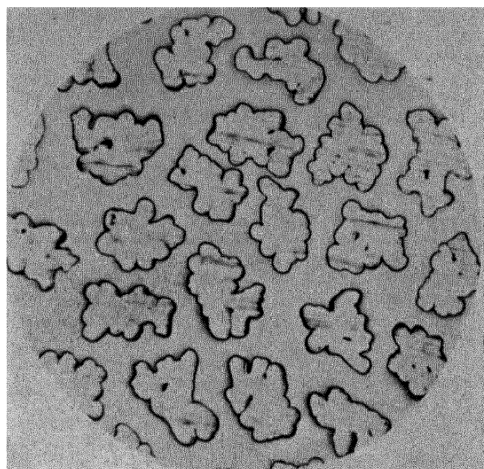
These boxes are then stacked in a room maintained at constant temperature, generally about 20° C., for a period of 54 to 72 hours, depending on the cellulose employed. During this maturing period further oxidation takes place, and the viscosity of the cellulose is progressively reduced. Exothermic reactions cause the temperature of the crumbs to rise, and it is for this reason that relatively small containers are used. Even so, it is not uncommon for the crumbs at the centre of a container to be at a temperature 2° to 3° C. higher than the atmosphere in the maturing room.

Temperature During Maturing.

The temperature during maturing has very considerable influence on the viscosity of the viscose obtained, as is shown by the following results of laboratory trials. Samples of pulp were processed with different maturing temperatures, but otherwise under identical conditions throughout, and the viscosities were determined with an Ostwald viscometer when the viscoses had ripened for 72 hours.

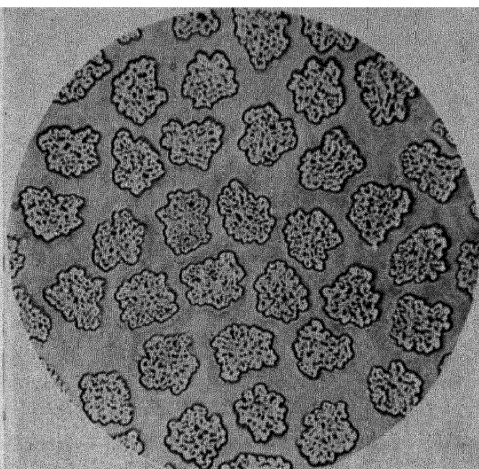
	Viscosity, in Centipoises.
Viscose from alkali cellulose matured at 10° C. ..	57.1
Viscose from alkali cellulose matured at 20° C. ..	20.7

Some workers claim to have dispensed with this maturing period, generally by the substitution of an equivalent oxidising



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Fig. 4.—TYPICAL CROSS SECTION OF NORMAL VISCOSE YARN.



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Fig. 5.—DULL LUSTRE YARN CONTAINING DISPERSED OIL PARTICLES.

process at some earlier stage. Oxidation alone, however, does not appear to be sufficient, and the addition of oxidising agents to the steeping liquor will not entirely duplicate the effects of the maturing period.

An Alternative Method.

An alternative method which has had some industrial success is based on the use of relatively heavily bleached pulp of low viscosity. In such pulps the cuprammonium viscosity may be as low as 12 centipoises, as compared with 24.8 centipoises for normal viscose pulp, as given on page 1407. As might be expected, the Beta cellulose content is high, reaching 7 per cent. or more. In this instance the "maturing" has really been achieved by the pulp producer, and any expense and loss in yield occasioned has fallen on him rather than on the viscose mill. However, in addition to these advantages, such pulps have considerable drawbacks, notably poor swelling factor and low reactivity, with resultant difficulties in viscose processing and relatively low wet strength in the yarn produced. It appears, therefore, that cumbersome and expensive as it is, the maturing period is likely to remain part of the viscose practice, at least until some new line of approach is discovered.

Formation of Cellulose Xanthate.

Although swollen in the mercerising

stage, and to some extent cut and broken during grinding, the ultimate fibres in the wood pulp have so far retained their identity. In the next stage, during the formation of cellulose xanthate, the fibres swell further to the point of dispersion, and cease to have separate existence. This is brought about by treating the alkali cellulose crumbs with carbon disulphide, in amount equivalent to about 33 per cent. calculated on the original weight of the cellulose present. This reaction is essentially between gaseous carbon disulphide and solid alkali cellulose, and if allowed to proceed too far results in the production of sticky agglomerates.

The Churns.

For this reason it is necessary to have continuous but gentle agitation, exposing fresh surfaces throughout the reaction period. The most usual device for this purpose is an hexagonal churn which slowly rotates. In some instances these churns are jacketed for temperature control, but generally it is considered sufficient to control the temperature of the room in which the churns are situated. In these circumstances the exothermic reaction taking place will cause a temperature rise of about 10° C. in three hours.

Time of Churning.

The churning time may be controlled by a fixed time schedule, the attainment

of a given temperature, the physical condition of the crumbs, or the colour of the xanthate, and an experienced worker will make use of a combination of these factors. The most commonly accepted single criterion, the colour of the xanthate, is probably the least reliable, since it is largely dependent on side reactions and by-products.

When the changes in cuprammonium viscosity of the cellulose are followed throughout the viscose process, it is found that although not the largest, certainly the most rapid fall in viscosity occurs during xanthation, and this indicates the need for careful control of this stage in relation to the final quality of the yarn, quite apart, also, from the difficulties which will otherwise arise in the viscose mill.

The Mixing Vessel.

When the xanthation is judged to be complete the excess carbon disulphide is removed by suction or pressure and the content of the churn transferred to a mixing vessel. The use of a single machine for both churning and mixing has many times been suggested, and recently plant similar to the usual grinding disintegrating machine has been used with apparent success.

Why the Xanthated Crumbs are not Dispersed in Water Alone.

The xanthated crumbs could now be dispersed in water alone, but a viscose produced in this way would be difficult to filter, with a very high viscosity, and would spontaneously regenerate in quite a short time. These factors are largely governed by the ratio of cellulose to soda present in the viscose. With viscose containing 7 per cent. of cellulose the point of minimum viscosity and maximum stability corresponds to a ratio of 1 to 1.1, as compared with 1 to 0.35 if the crumbs are dispersed in water without any additional soda. In rayon practice the lowest ratio normally encountered is about 1 to 0.65, and is generally more of the order of 1 to 0.9. Low soda content will also mean low consumption of sulphuric acid in spinning, but the apparent saving may well prove expensive, due to viscosity variations and difficulties in controlling speed of ripening.

The Caustic Soda Solution.

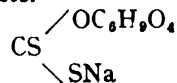
The cellulose xanthate is, therefore, dispersed in caustic soda solution, often containing also some sodium sulphite, in mixers, so that the final viscose contains approximately the following proportions:

	Per cent.
Cellulose	7 to 8
Total caustic soda	5.5 to 6.5
Sodium sulphite	0.75 to 1.0

After mixing the viscose is pumped to storage containers maintained at constant temperature and in which the ripening process is allowed to proceed to the point required for spinning.

Ripening.

The new viscose, when first prepared, cannot be easily regenerated since it contains a high proportion of sodium cellulose xanthate.



and relatively little free cellulose. This sodium cellulose xanthate slowly decomposes, increasing the amount of free cellulose. Thus as ripening proceeds the proportion of cellulose to protective colloid or dispersing agent increases, making coagulation less difficult until finally in the extreme the cellulose is spontaneously regenerated.

Viscosity Changes.

Viscosity changes also occur during this period. The viscosity at first falls steeply, probably due to osmotic effects causing water to pass from the internal to the external phase, and subsequently rises, due to the decomposition of the xanthate and an increasing proportion of free dispersed cellulose. Close control of the ripening process, and indeed much of the control of the earlier processes, is necessary to obtain simultaneously the required viscosity and coagulation characteristics. Viscosity changes can be followed by any of the normal methods, the ball fall being the most usual.

The ease of coagulation, or "degree of ripening" of viscose can be estimated by methods depending either on direct coagulation or on the determination of the amount of sodium cellulose xanthate still remaining.

Direct Coagulation.

For direct coagulation either sodium

chloride or ammonium chloride can be used, and probably the ammonium chloride method has the least personal factor and is in most general use. A standard quantity of viscose, usually 20 gm., is diluted with water to a final cellulose concentration of 3 per cent., and is then titrated with 10 per cent. ammonium chloride solution. The number of cubic centimetres

required to cause coagulation to commence is taken as an index of the degree of ripening. Dependent on the treatment given to the cellulose during the earlier stages, the proportion of caustic soda in the viscose, and similar considerations, the amount of ammonium chloride solution required by a new viscose in the above test may be from 12 to 15 cubic centimetres. With ripening temperatures of 16° to 17° C. the viscose will reach the condition required for spinning, corresponding to an ammonium chloride solution requirement of 7 to 8 cubic centimetres, in 92 to 96 hours.

Determination of Sodium Cellulose Xanthate Content.

The sodium cellulose xanthate content may be estimated by titration with iodine or by determining the amount of sulphur present in combination with the cellulose. The total iodine requirement of the viscose is estimated by the addition of excess and back titration with N/10 sodium thiosulphate. The cellulose xanthate is precipitated from another viscose sample by the addition of saturated sodium chloride solution and the iodine requirement of the separated liquor determined. The difference between the two values thus obtained is indicative of the amount of cellulose xanthate present.

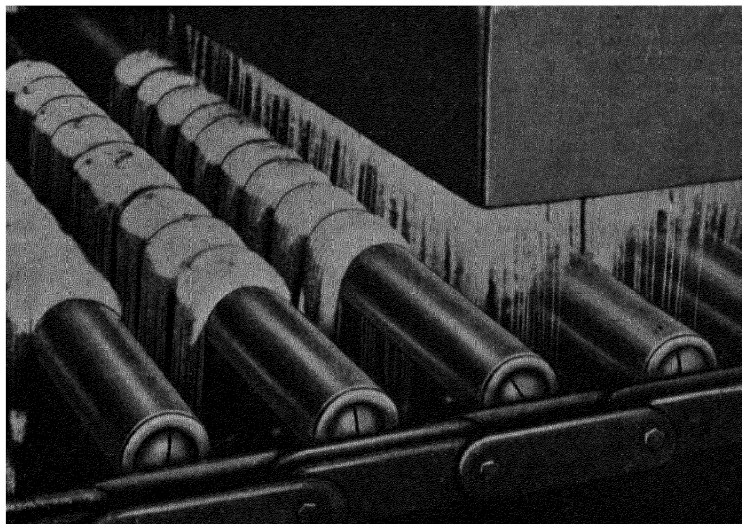


Fig. 6.—HANK WASHING MACHINE..

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The Total Sulphur Content.

Alternatively, the total sulphur content can be determined, and also the sulphur content of the liquor remaining after salting out the cellulose xanthate, thus by difference giving the amount of sulphur combined with the cellulose.

The results from either of these methods can conveniently be expressed in terms of "xanthate soda," that is, the amount of sodium combined as xanthate with 100 gm. of cellulose when calculated as percentage NaOH. Xanthate soda values between 8 to 10 per cent. are commonly obtained with ripened viscose which is ready for spinning.

Delivery of Viscose to Containers.

During the 92 to 96-hour ripening period the viscose is freed from occluded air bubbles, and after passing through a succession of filter presses is delivered to containers from which the spinning machines are fed. Viscose at the correct salt number is then pumped to the spinning machine, and, having been forced through the candle filters, is delivered into the coagulating acid bath through jets, in each of which there are a number of holes of the order of 0.1 millimetre in diameter.

The Acid Spinning Bath.

Variations in the composition of the acid spinning bath have been the subject

of an enormous number of patents, but it is probable that only quite a few materials are actually in commercial use for the purpose. Sulphuric acid of 8 to 10 per cent. concentration performs the double function of decomposing the sodium cellulose xanthate and neutralising the caustic soda present. Obviously sodium sulphate (or bisulphate), is formed during the reaction, but additional sodium sulphate up to about 14 per cent. on the solution is also usually present.

Cross Sections.

The type of cross section required in the final yarn governs the addition of other constituents, and for the production of the usual serrated cross section about 1 per cent. of zinc sulphate is commonly employed. In addition materials which will retard the crystallisation of salts in the threads may be present, and glucose is, or was, used in this connection.

Immersion of Viscose in Acid Solution.

When the fine stream of viscose comes into contact with this solution having high acid and salt concentration both decomposition and salting out of the xanthate take place on the outer surfaces exposed. These reactions result in the production of a surface skin, which much reduces the speed of penetration into the centre of the filament. With such normal conditions as an immersion distance in the setting bath of say 12 in., and a speed of 150 ft. per minute, the total immersion time is less than half a second. However, as the thread travels upwards to the godet and down into the spinning box it carries with it a quantity of the setting bath, and neutralisation and coagulation continue under these conditions.

A Typical Example.

This is clearly shown by the lower acid concentration found in such drainage liquor, as compared with the original setting bath from which it is derived. In a typical instance the filaments were withdrawn from a bath containing 8.5 per cent. sulphuric acid and 14 per cent. of sodium sulphate, but the liquor recovered from the thread contained only 5.7 per cent. of acid, and the sodium sulphate content had increased to 16 per cent.

Storage of Cakes of Thread.

The cakes of thread which are removed from the spinning box may still contain as much as 3 per cent. of sulphuric acid, and it is imperative that the outer layers should not be allowed to dry during the period which must elapse before reeling. The cakes are, therefore, stored in chambers in which the atmosphere is maintained at as near as possible to 100 per cent. relative humidity.

In recent years there has been a tendency towards the use of the cakes direct for the finishing processes, eliminating reeling, but a large quantity of thread is still finished in the hank condition. Formerly the skeins were washed and dried under tension before going forward to the finishing processes, but this intermediate drying operation is now frequently omitted.

Desulphuring.

The skeins are hung on smooth ebonite rods which carry them through a succession of baths intended to remove by-products remaining from the spinning process and improve the colour of the thread. If the thread has not previously been washed it is first passed through water sprays to remove the acid and salts remaining from the spinning bath. During the coagulation of the thread, sulphur is precipitated, and to remove this the skeins are next treated with sodium sulphide solution, using concentrations between 1 and 2 per cent., and a temperature of about 50° C. Under these conditions sodium sulphide readily removes this sulphur in the form of polysulphides. Thus the solution will become rich in sulphur, but this tendency may be counteracted by the addition of alkali together with a reducing agent such as glucose, resulting in the conversion of the polysulphides to monosulphide, thus maintaining the content of effective agent in the solution.

Washing.

Following desulphuring, the skeins are water washed and then passed to the bleaching baths. In view of the relatively sensitive condition of the cellulose the bleaching must be carried out under closely controlled conditions designed to minimise attack upon the thread. An alkaline hypochlorite solution is therefore

employed, containing only about 0.1 per cent. of "available chlorine," and the temperature is kept low, between 20° and 25° C. After bleaching, the skeins are soured by immersion in dilute acid solution, generally hydrochloric acid of from 0.5 to 0.75 per cent. concentration, and, following further water washing, are treated with a warm soap solution which may also contain one of the sulphonated dispersion agents.

A considerable quantity of rayon is also marketed in the unbleached condition, and this thread passes through identical finishing processes, with the exception of

the bleaching stage. From the point of view of cellulose quality this is an important omission, resulting in better retention of cuprammonium viscosity and strength in the final thread.

After soaping, the skeins are charged to centrifugal hydro-extractors, which eliminate about four-fifths of the original water content, and the remaining water is removed by drying at low temperature. The skeins are then allowed to come into equilibrium with an atmosphere maintained at a controlled relative humidity, and after sorting are ready for the mechanical textile processes.

THE CONTROL OF TEMPERATURE IN AIR DRYING OVENS

THE temperature can be controlled by connecting the heating elements into two circuits through a rotary heater switch, which is marked HIGH—MEDIUM—LOW, and can be rotated to the desired marking.

What the switch does on "High" is to put both the heating circuits ON. On "Medium" only one circuit is on, which reduces the heat generated to half, and on "Low," both heater circuits are connected in "Series" which reduces the heat to a quarter of that generated on "High." This form of control is obviously very coarse.

Finer control can be obtained by using a rheostat or regulating resistance, which can be adjusted to reduce the current passing through the heaters, in other words it dims the heaters down to the temperature required.

The most satisfactory method, however, is by a well-designed automatic thermostat arrangement.

The two heating elements and thermostat must be designed to work together if very close temperature control is to be

obtained. The thermostat, of course, is an instrument which switches off the heat, when the desired temperature is reached, and on again when the temperature falls slightly below.

It is not advisable to make the thermostat switch the total number of heating elements off, otherwise the temperature fall too will rapidly, and several degrees drop will take place before the thermostat switches the heaters on again.

It is best to leave on permanently sufficient heaters nearly to maintain the desired temperature, and make the thermostat automatically switch in and out a small heater of sufficient power to bring the temperature up to the final value.

This controlled element should be as far as practically possible "lagless," that is, it should heat up immediately it is switched on, and lose its heat immediately it is switched off, similar to the filament inside the electric lamp.

The thermostats generally used are operated by either a compound strip of two dissimilar metals, or by the expansion of a metal tube.

THE INDIA RUBBER INDUSTRY

PART II.—THE ANALYSIS AND TESTING OF RUBBER LATEX

By J. R. SCOTT, Ph.D., F.I.C.

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IN a previous article it has been explained that the "latex" obtained from the rubber tree is a milky suspension of minute rubber particles in a watery "serum." In addition to being the starting point for the preparation of crude rubber, latex is now used directly in the manufacture of many rubber goods and also in other industries as an adhesive, sealing composition, coating or impregnating material, etc. The uses of latex are multiplying and developing so rapidly that it is important for the chemist to know something of the methods used in its examination.

Commercial Types of Latex.

The four main types of latex with which the chemist may be called upon to deal are :—

(i) Preserved latex, i.e. latex of normal strength containing a little ammonia as a preservative and anti-coagulant.

(ii) Concentrated latex, in which the rubber content has been increased by removing some of the water, usually by evaporation or centrifuging; a preservative, e.g. ammonia, and/or protective colloids are usually added to prevent coagulation.

(iii) Com-
pounded latex,
containing
some of the

numerous "compounding ingredients" used to give the finished rubber its desired properties, e.g. sulphur to effect vulcanisation, organic "accelerators," mineral fillers, pigments, etc. (the nature and functions of these materials have been discussed in a previous article); protective colloids are almost always added at the same time to prevent coagulation.

(iv) Vulcanised latex, in which the rubber particles have been vulcanised by adding sulphur and an accelerator and heating under such conditions as to prevent coagulation.

It will be understood that some of the above-mentioned treatments may be combined; thus, we may have concentrated compounded latex, concentrated vulcanised latex, compounded vulcanised latex, etc.

Before describing in detail the various tests commonly applied to latex it will be helpful to give some explanation of the reasons for applying these tests.

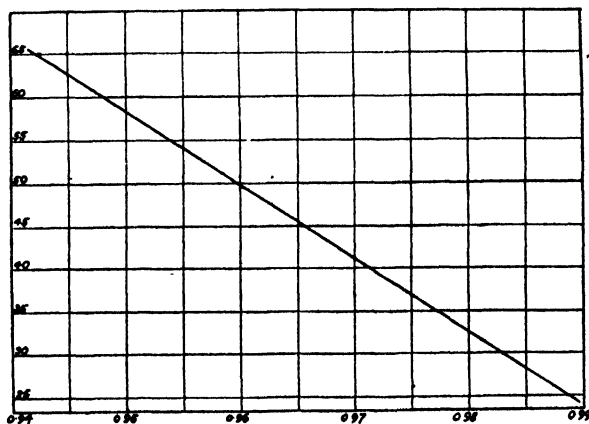


Fig. 1.—GRAPH SHOWING THE RELATIONSHIP BETWEEN SPECIFIC GRAVITY AND DRY RUBBER CONTENT OF PRESERVED LATEX.

Specific Gravity

With ordinary ammonia-preserved latex (not compounded or vulcanised) the specific gravity is approximately related to the rubber content, for which reason specific gravity is often used as a quick rough method of estimating the rubber content.

The relationship between these quantities is expressed mathematically by the following equation :—

$$S = 1.0177 - 0.001158 R$$

where S is the specific gravity at 29° - 30° C., and R is the rubber content as a percentage by weight.

Owing to the variation in the amounts of non-rubber solids dissolved in the serum and of added ammonia, the gravity-rubber content relation is not exact, so that specific gravity measurements cannot be relied upon where an exact knowledge of the rubber content is required.

Total Solids.

Most of the solid matter present in latex is rubber, and hence the "total solids" represents an approximate measure of rubber content. As, however, a portion of these solids (about 10 per cent. in the case of normal latex) represents water-soluble substances which do not appear in the dry rubber as ordinarily prepared, the results given by this method are correspondingly too high.

Dry Rubber Content.

This represents the amount of dry rubber obtainable from the latex by the usual method of preparation. As latex is bought and used solely on account of the rubber which it contains, the importance of the "dry rubber content" is obvious.

Ammonia Content.

The ammonia used to preserve the latex, during shipment from the plantation to the manufacturer, affects its subsequent processing; a knowledge of the ammonia content is therefore essential to successful working.

Hydrogen-Ion Concentration.

As latex is a colloidal system its behaviour depends greatly on the hydrogen-ion concentration (pH) of the aqueous phase or "serum"; hence, for certain processes in

which latex and latex compositions are used, these must be brought to the correct pH value.

Viscosity.

In using latex and latex compositions for such processes as "spreading" on fabrics and making rubber articles by "dipping" (these processes have been described in a previous article), correct viscosity is essential to obtain a satisfactory coating on the fabric or to ensure the correct thickness of deposit on the dipping form.

Compounded Latex.

In the case of compounded latex it may be desired to know the amount and nature of the compounding ingredients (i.e. non-rubber materials) added. This is done by evaporating the latex to dryness as described below under "Total Solids," and then analysing the dry residue by the methods applied to vulcanised rubber.

It must be emphasised that the commercial use of latex is of such recent development that the methods of analysis and testing have not yet become standardised. Those described below are methods developed and used by competent authorities, but do not represent universally adopted practice.

METHODS OF ANALYSING AND TESTING.

Sampling.

When latex is allowed to stand, the rubber particles, being lighter than the watery "serum" in which they are suspended, tend to rise to the top ("creaming"). In compounded latex, for a similar reason, the mineral ingredients tend to settle to the bottom. Before test samples are taken, therefore, the latex must be rendered homogeneous by gently stirring it for several minutes; violent agitation must be avoided, as it may lead to coagulation or clotting.

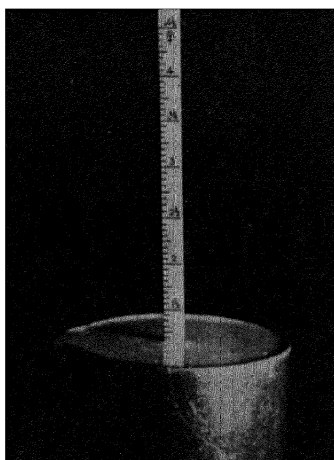


Fig. 2.—MEASURING THE DRY RUBBER CONTENT OF LATEX BY MEANS OF THE "METROLAC."

This is a special type of hydrometer graduated in lbs. of rubber per gallon. The instrument is indicating 1 lb. 2 ozs. per gallon, or about 11 per cent. of rubber by weight.

As the latex dealt with in manufacturing countries normally contains ammonia, care must be taken not to expose test samples to the air unnecessarily, as the resulting loss of ammonia may vitiate the results or cause premature coagulation.

Any small clots or lumps in the latex should be strained off before sampling.

Specific Gravity.

This is most conveniently measured by a hydrometer of the usual spindle type. For use with ordinary latex this should be graduated from about 0.90 to 1.00; compounded latex, being usually denser, requires a scale extending to higher values (say, about 1.3 maximum).

As hydrometers are in common use in chemical laboratories, no detailed description of the method of use need be given here.

For measuring the rubber content of uncompounded latex, there are special types of hydrometer (such as the "metrolac" and the "latexometer") graduated to indicate directly the rubber content of the latex in lbs. per gallon.

Total Solids.

A flat-bottomed glass dish is weighed, and sufficient latex is poured in to cover the bottom with a thin layer, the weight of the latex being determined by a second weighing; not less than 10 gm. of latex should be taken. The water contained in the latex is then dried off by heating the dish at 100° C. until constant weight is attained.

If a small rubber mixing mill (or any pair of rollers suitable for sheeting out materials) is available, the drying may be hastened by removing the partially dried layer of rubber, as soon as it forms a coherent sheet, and rolling it out thin on the mill before continuing the drying.

The weight of the final dry residue, expressed as a percentage of the weight of latex taken, represents "total solids."

Dry Rubber Content.

The latex (about 25 c.c.) is weighed out into a porcelain basin. In the case of concentrated latex of over 50 per cent. rubber content, it should be diluted with an equal volume of distilled water. Dilute acetic acid (1 per cent.) is now added slowly with constant stirring until

the latex appears to be coagulated and further addition produces no apparent effect. The amount of acid required varies according to the latex, and can best be judged by a little practice.

The basin is placed on a steam-bath and left undisturbed for half an hour. The rubber will then have completely separated as a coherent clot or "coagulum," leaving a clear watery "serum," which is poured off and replaced by clean water.

Sometimes a small amount of the rubber (not more than a fraction of 1 per cent. reckoned on the latex) remains suspended in the serum as small flocks. These can be filtered off on a tared filter paper, which is then washed, dried, and weighed.

The main coagulum is rolled out into as thin a sheet as possible on a hard smooth surface, then washed in running water for an hour, to remove adherent and entrapped serum, and finally dried at 100° C. (steam oven) until constant in weight; 2-3 hours' drying usually suffices.

If a crêping mill is available, it is preferable to wash the coagulum thoroughly by passing it repeatedly between the rollers of the mill under a stream of water. During this operation the rollers are gradually brought closer together, so that finally the coagulum forms a thin "crêpe" sheet, which is then dried as described above.

The weight of the dried rubber, expressed as percentage of the weight of latex taken, represents the "dry rubber content."

Ammonia Content.

Exactly 10 c.c. of latex is measured out and diluted with distilled water up to 250 c.c. From the diluted latex 25 c.c. is measured out with a pipette and titrated with N/10 hydrochloric acid. Methyl red is used as the indicator, being either added to the diluted latex, or preferably used as an external indicator. The acid is run in from the burette until the original yellow colour of the indicator changes to the orange characteristic of neutrality.

It is customary to express the ammonia content as grams per 100 c.c. of the original latex. Each c.c. of N/10 acid used corresponds to 0.17 gm. of ammonia per 100 c.c. of latex.

Hydrogen-Ion Concentration (pH).

This can be measured by means of indicators of the type used in connection with the familiar "comparator" and "capillator" sets. The pH range of natural latex (i.e. containing no ammonia) is about 6 to 7, and that of ammonia-preserved latex about 8 to 11. As the general principles of the use of such indicators for pH measurement are familiar to all chemists, it is only necessary to describe the special precautions needed when working with latex.

A rapid, though only approximate, method of pH measurement consists in applying a small drop of indicator solution to a filter-paper, and then applying a large drop of the latex on top of this. The colour of the indicator can then be observed on the reverse side of the filter-paper.

The more accurate measurement of the pH of latex depends for its success on the preparation of a clear "serum" by filtering off the rubber particles present in the latex. For this purpose 50 c.c. of latex are mixed with 0.5 gm. of gas black (the extremely finely divided carbon made by the combustion of natural gas) and 20 c.c. of the mixture are filtered under a pressure of 15 lb./in.² through a special filter. This is made by pouring a mixture of cellite and water on to a filter-paper in a small Buchner funnel, washing well with water by suction, and drying at 100° C.

During the filtration of the latex mixture

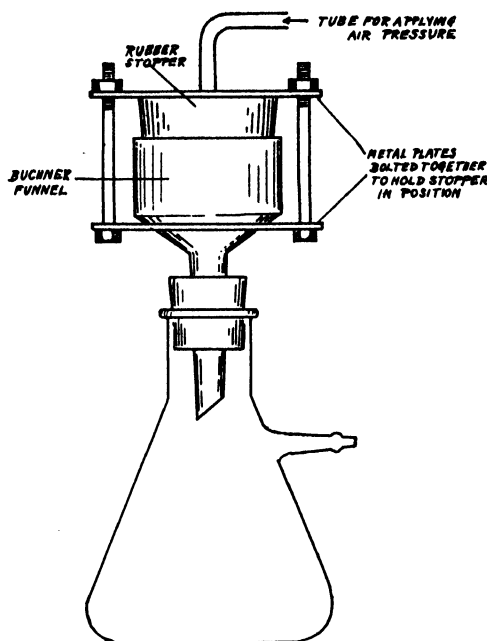


Fig. 3.—APPARATUS FOR FILTERING LATEX PRIOR TO THE DETERMINATION OF pH VALUE.

the funnel is closed by a rubber stopper held tightly in position by two metal plates bolted together (see Fig. 3), and air pressure is applied through a tube in the stopper. Pressure must be used for the filtration, instead of suction, in order to minimise loss of the ammonia normally present in commercial latex.

The pH of the filtrate or "serum" is determined by the normal comparator method, about 2 c.c. being used for each determination.

Viscosity.

This is conveniently measured by means of a Red-

wood oil viscometer in which the usual agate jet is replaced by a stainless steel jet. To cover the whole viscosity range of latex and latex compositions a set of four jets respectively $1\frac{1}{8}$ ", $\frac{1}{8}$ ", $1\frac{3}{8}$ " and $\frac{1}{4}$ " in bore, the length being $\frac{1}{2}$ " in each case, has been recommended. To measure viscosity with this apparatus the latex is poured into the standard cylindrical cup ($1\frac{1}{8}$ " diameter) to the standard depth of $3\frac{1}{2}$ " above the top of the jet, which meanwhile is closed by the ball-shaped valve. After the latex has been brought to a standard temperature (20° C. is recommended) the valve is lifted to allow the latex to flow through the jet into a flask placed beneath. This flask has a mark on the neck corresponding to a volume of 50 c.c. The time required for the flask to fill up to this mark is measured. This time, expressed in seconds, is taken as a measure of the viscosity.

CHEMISTRY IN THE STUDY OF DISEASE

PART III.—THE BLOOD

By SIDNEY L. TOMPSETT, Ph.D.(Glas.), B.Sc.(Lond.), A.I.C.

Normal Composition.

The following is a list of the normal constituents of blood:—

Hæmoglobin	13-15 gm. per 100 ml.
Hydrogen ion concentration	7.4
<i>Whole Blood.</i>	
Protein :	<i>Plasma.</i>
Albumin	4.5-5.2
Globulin	1.9-2.6
Fibrinogen	0.2-0.4
	gm. per 100 ml.
Non-protein N ..	20-40
Urea	20-40
Uric acid	2-4
Sugar	80-100
Inorganic P. ..	2-4
Chloride (as NaCl)	450-530
Sodium	170-225
Potassium	150-250
Calcium	4-5
	mg. per 100 ml.
	9-11

It will be apparent that many of the constituents of blood are not equally distributed between the cells and the plasma, e.g., the plasma contains a higher concentration of chlorides than the cells, while most of the potassium is found in the cells, where it is combined with hæmoglobin as a protein salt. Calcium is present only in the plasma. With the exception of sugar, the concentration of the above substances vary very little in

health and are unaffected by meals. On the other hand, the concentration of sugar is increased after a meal containing carbohydrate.

By following the concentration of sugar in the blood after the ingestion of 50 gm. of glucose, such conditions as diabetes mellitus and renal diabetes may be differentiated. The curves, which are from typical cases, explain themselves.

The Collection of Blood.

The estimation of any of the constituents of blood naturally involves the use

of micro-methods. For most estimations, 5-10 ml. of blood are ample, this being obtained with a syringe and needle from the vein at the junction of the elbow. When whole blood is required, the blood is emptied into a tube containing 0.1 gm. of potassium oxalate and vigorously shaken to prevent clotting. In estimations, e.g., calcium, where serum is required, the blood is allowed to clot, then centrifuged and the clear supernatant serum

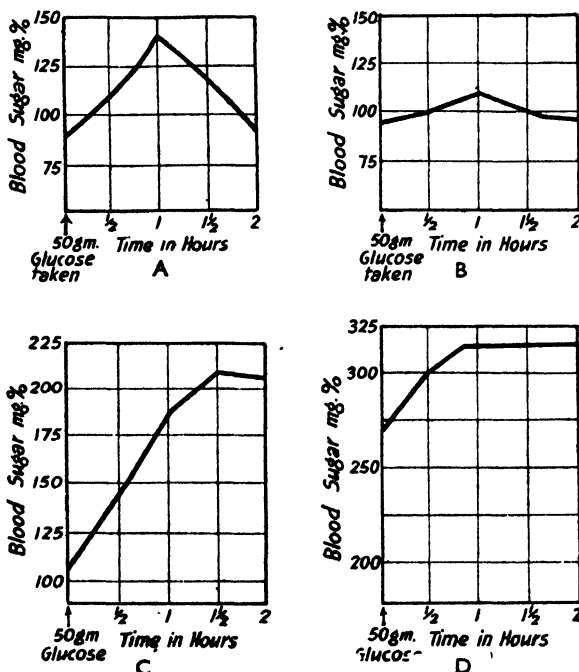


Fig. 1.—CURVES FROM TYPICAL CASES OF DIABETES MELLITUS AND RENAL DIABETES.

A, Normal; urine passed during experiment will give negative tests for sugar. B, Renal diabetes; urine may give positive test for sugar. C, Mild case of diabetes mellitus; urine will probably contain sugar. D, Severe case of diabetes mellitus; urine will give strong positive tests for sugar.

removed with a teat pipette. Methods have been evolved whereby sugar can be accurately estimated in 0.1 and 0.2 ml. of blood. In this case the blood is drawn from a prick in the ear or thumb into a special micro-pipette and then blown into the diluting fluid.

With the exception of sugar, the constituents of blood are stable after their removal from the body. The estimation of sugar must be proceeded with as soon as the blood has been taken, since it is decomposed fairly rapidly by glycolytic ferments.

THE DETERMINATION OF BLOOD UREA.

The blood is incubated with powdered soya bean, which contains an enzyme urease. The urea is converted into ammonium carbonate by the action of this enzyme. The ammonia so formed is determined colorimetrically with Nessler's reagent.

Into a test tube are measured 4 ml. of 0.6 per cent. acid potassium phosphate, followed by 2 ml. of oxalated blood. After the addition of 0.2 gm. soya bean meal, the mixture is incubated at 37° C. with frequent shaking for 30 minutes. To the mixture, are now added 10 ml. of water, followed by 2 ml. of 10 per cent. sodium tungstate. After mixing, 2 ml. of N. sulphuric acid are added and the whole well mixed. The proteins are precipitated by this procedure and on filtration, a water clear fluid is obtained.

In the apparatus shown in Fig. 2, the ammonia is distilled off and trapped in acid, 5 ml. of the filtrate are measured into the 8 × 1 inch test tube followed by 2 ml. of saturated borax (to liberate the ammonia), and a few drops of liquid paraffin.

A glass bead should also be added to prevent bumping. The apparatus is fixed up as shown. The receiver, a test tube with a mark at 25 ml., contains 2 ml. of N. sulphuric acid. The liquid paraffin and the spiral of galvanised iron wire are to prevent frothing. The mixture in the tube is now heated by the micro-burner. As soon as the volume of fluid in the receiver is doubled, the delivery tube is separated from the distilling tube and washed into the receiver.

The contents of the receiver are now thoroughly cooled, 10 ml. (about) of distilled water added, followed by 5 ml. of Nessler's reagent and then diluted to 25 ml. After mixing the solution is compared in a colorimeter with a standard.

Preparing the Standard.

The standard is prepared by measuring 3 ml. of ammonium sulphate solution (0.4716 gm. per litre) into a 100 ml. volumetric flask containing about 70 ml. of water, 10 ml. of Nessler's reagent are added and the mixture diluted to the mark with distilled water.

When the standard is set at the 20 mark in the colorimeter, the reading of the unknown divided into 642.8 will give the mg. of urea in 100 ml. of the blood under analysis.

What the Test Shows.

When the blood urea is high, turbidities will occur on the addition of Nessler reagent and so the estimation must be repeated, using a smaller volume of filtrate.

A high blood urea indicates disease of the kidneys, e.g., Bright's disease. Values as high as 300-400 mg. per 100 ml. may be obtained in such conditions and are due to the inability of the kidney to excrete this waste material.

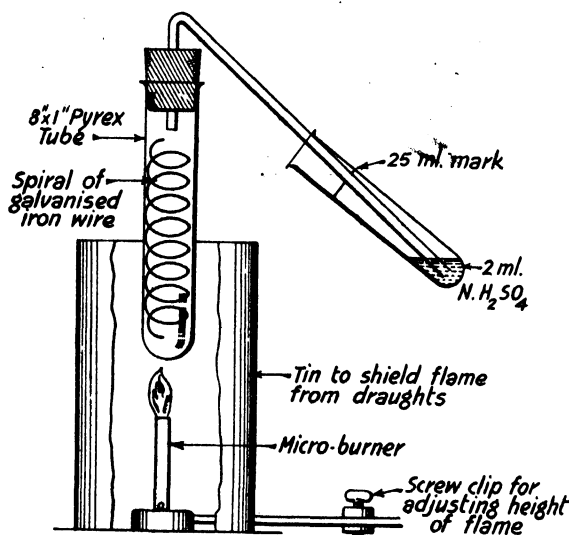


Fig. 2.—APPARATUS FOR THE DETERMINATION OF BLOOD UREA.

THE ESTIMATION OF BLOOD SUGAR.

Solutions Required.

(1) 10 per cent. sodium tungstate ;
 (2) 0.66 N. sulphuric acid ;
 (3) Alkaline copper reagent. Dissolve 40 gm. of anhydrous sodium carbonate in about 400 ml. of distilled water and add 7.5 gm. of tartaric acid. When the tartaric acid has dissolved, add 4.5 gm. of crystalline copper sulphate dissolved in 100 ml. of water and dilute the mixture to 1 litre.

(4) Phosphomolybdic acid reagent. Dissolve 35 gm. of molybdic acid and 5 gm. of sodium tungstate in 200 ml. of 10 per cent. sodium hydroxide and boil for 40 minutes. Cool, dilute to about 350 ml. with water, add 125 ml. of 85 per cent. syrupy phosphoric acid and dilute to 500 ml. with water.

(3) Glucose standard solution. Dissolve 0.1 gm. of pure anhydrous glucose in saturated (2.5 per cent.) benzoic acid solution and dilute to 100 ml. with this solution. This solution of glucose will keep indefinitely. [Stock Solution.]

Before use, the standard glucose solution for the actual estimation is prepared by diluting 5 ml. of the above to 100 ml. with distilled water. (1 ml. of this solution contains 0.05 mg. glucose.)

The Principle of the Estimation.

The blood proteins are precipitated with tungstic acid and an aliquot of the protein free filtrate heated with an alkaline copper reagent under standard conditions. On the addition of phosphomolybdic acid reagent, this is reduced to an intensely blue derivative by the cuprous oxide. The intensity of the colour is compared in a colorimeter with a standard solution

of glucose which has been treated similarly.

Method.

Into a 10 ml. centrifuge tube, measure 3.5 ml. distilled water. Then add 0.1 ml. of freshly drawn blood. Water is drawn up into the pipette and blown back into the tube several times (because blood is a "sticky" substance). Then 0.2 ml. of tungstate solution, followed by 0.2 ml. of $\frac{2}{3}$ N. sulphuric acid are added with micro-pipettes. After mixing the contents of the tube are centrifuged at 2,000-3,000 r.p.m.

Three Folin sugar tubes are now taken, two for the standards and the other for the blood.

Into one tube measure 2 ml. of protein free blood extract. Into the other two tubes add as follows : (a) 1 ml. dilute glucose standard solution and 1 ml. distilled water ; (b) 2 ml. dilute glucose standard solution.

To all three tubes add 2 ml. of alkaline copper solution and place in a boiling water bath for exactly six minutes. At the end of six minutes cool and add 2 ml. phosphomolybdic acid reagent, and dilute each to the 12.5 ml. mark with distilled water.

The unknown is compared in a colorimeter with that

standard which it approximates to mostly. It is usual to set the standard at 40 in this estimation.

Calculation.

Using standard (a), the reading of the unknown divided into 4,000 = mg. glucose per 100 ml. blood.

Using standard (b), the reading of the unknown divided into 8,000 = mg. glucose per 100 ml. blood.

HÆMOGLOBIN.

In arterial blood, the hæmoglobin is in

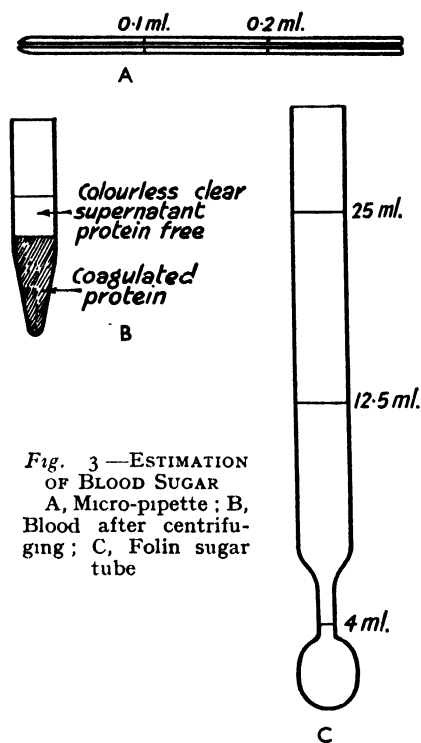


Fig. 3 — ESTIMATION OF BLOOD SUGAR
 A, Micro-pipette ; B, Blood after centrifuging ; C, Folin sugar tube

the form of a loose compound with oxygen known as oxyhæmoglobin. The hæmoglobin of the blood in the veins is in the reduced form, but when collected in a tube it quickly absorbs oxygen from the atmosphere.

When an oxidising agent, e.g., potassium ferricyanide, is added to reduced or oxy- hæmoglobin, an "oxide" known as methæmoglobin is formed. It has a dark brown colour in contrast to the red colour of oxy- and the purple colour of reduced hæmoglobin. Whereas the oxygen of oxyhæmoglobin is removed by subjecting it to a vacuum, that of methæmoglobin is only removed by the action of such reducing agents as sodium hydro-sulphite and ammonium sulphide. For such reasons methæmoglobin is inefficient as a carrier of oxygen in the body. It is found in the blood and sometimes in the urine in aniline poisoning, hence some of the symptoms.

When carbon monoxide (coal gas, etc.) is passed into a solution of any of the above pigments, carboxyhæmoglobin, a substance with no respiratory properties is formed. This is a very stable compound and is unaffected by a vacuum and reducing substances. Owing to this great stability, carbon monoxide is very poisonous and in severe cases always leaves some mental instability.

When a weak acid, e.g., acetic acid, is added to a solution of oxy- or methæmoglobin, the protein, globin is split off to leave hæmatin which contains oxygen combined as an oxide. Treatment with reducing agents gives reduced hæmatin. Hæmatin is soluble in and may be extracted by ether (note confirmatory test for blood in urine). It will be noted that the removal of protein from the oxyhæmoglobin molecule causes the oxygen to be more strongly combined, i.e., to form an oxide. Hæmatin is not found free in the body.

By the action of strong acids on hæmoglobin, e.g., concentrated sulphuric acid, the iron as well as the protein is split off, and a pigment hæmatoporphyrin is left. This substance has no power of combining with oxygen. All the

above compounds with the exception of this latter, give a positive test with guaiacum and hydrogen peroxide, i.e., all those containing organically combined iron. Hæmatoporphyrin is sometimes found in the urine of certain persons who are susceptible to the action of such drugs as sulphonal, trional, veronal, etc.

When solutions of the above pigments are viewed through a spectroscope, absorption bands typical of the pigment will be observed. It will be observed that in the case of such pigments as hæmatin, hæmatoporphyrin, the position of the bands depends on the reaction of the solution, i.e., acid or alkaline.

Examination of Blood for the Presence of Carboxy- or Met- Hæmoglobin.

Blood is opaque to light but on the addition of water the cells burst and a clear solution is obtained. This is diluted so that the absorption spectrum may be observed clearly.

Even in the presence of oxyhæmoglobin, certain of the typical bands of methæmoglobin may be observed if this substance is present. To confirm, these bands should disappear on the addition of hydro-sulphite, the bands of reduced hæmoglobin being formed.

Bloods containing the carboxy derivative remain persistently pink on dilution, whereas normal blood under the same conditions turns brown. Carboxy hæmoglobin has a similar picture to that of the oxy compound but may be differentiated by adding hydrosulphite to the solution when the bands due to the former will still persist.

Examination of Urine for Methæmoglobin and Hæmatoporphyrin.

In the case of the former the same technique is used as with blood.

When present in urine, the bands of alkaline hæmatoporphyrin are observed. To confirm, strong HCl is added to the urine followed by amyl alcohol and the whole shaken. After centrifuging, the bands of acid hæmatoporphyrin should be seen in the amyl alcohol layer.

SYNTHETIC RESINS

PART II.—RESORCINOL, UREA AND CUMARONE RESINS

By H. COURTNEY BRYSON

Resorcinol Resins.

RESINS may be produced from the higher phenols such as butyl phenol, and possess characteristics making them useful as varnish media. In addition, the phenolic body known as dihydroxy benzene or resorcinol, yields resins with extraordinarily interesting properties. Up till a year or so ago, resorcinol was only produced commercially on the Continent and in America. The reaction between resorcin and formaldehyde is much more vigorous than the corresponding reaction with phenol, and the difficulty is usually experienced in preventing it from carrying through with premature spontaneity. The reaction is, therefore, normally carried out in solution in order that it may be controllable. When resorcinol drops in price, the resin will doubtless be used as a constituent of quick moulding powders.

Unbreakable Gramophone Records.

One of its most interesting uses has been for the production of unbreakable gramophone records, such as the Durium record and the Worldcho record. Equal parts of resorcinol and formaldehyde with about $1\frac{1}{2}$ per cent. sodium sulphite are warmed in alcohol to a temperature of 70° C. for a time depending on the bulk of the batch.

Control of the Reaction.

The reaction must be closely controlled if consistency is to be attained, and since it is easier to control a small batch than a big one, many small batches should be made and averaged. The solution of resin thus obtained increases in viscosity at room temperature even if kept in a stoppered bottle to prevent evaporation of alcohol, till eventually the final infusible C state occurs spontaneously. The very largest sized batch possible is one of about 20 gallons and a pan possessing a water-

jacket with forced circulation of water must be employed to control the reaction.

Preparation of Impregnated Sheets.

As soon as the resin is ready it is used to impregnate special paper, the process being done on a paper coating machine where a coat of given thickness is spread on the paper from a roll by means of a doctor. The paper is dried in a drying tunnel and then cut into sheets.

During the drying process great care must be exercised to see that only sufficient heat is applied to drive off the solvent and that the resin is not cured. The dried impregnated sheets are placed on top of card-backing sheets and then placed between the platens of a heated press.

Pressing the Record.

Automatic presses of the cam type, such as are used for gold-blocking are best employed and from four to six single-sided records can be pressed at a time, the complete pressing cycle taking about three seconds.

The Stampers.

The stampers, of nickel-plated copper, containing the sound grooves are fixed to the upper platen and heated, generally by electricity, to 180° C. The curing of the resin is practically instantaneous. In fact, if it is not instantaneous the record will be worthless. In order to obtain standard results, efficient control at every stage of the process is essential. Records of this type suffer from needle drag and substances such as soap and the like may be introduced in order to decrease the coefficient of friction between record surface and needle.

Urea Resins.

Resin of the phenol or cresol formaldehyde type suffer from the grave disadvantage that initially they are not pale in

colour and on ageing they darken. White moulded compounds cannot, therefore, be obtained from them. On the other hand, although the resins prepared by condensing urea $\text{CO}(\text{NH}_2)_2$ with formaldehyde are almost water white in colour, their technical preparation is more difficult and the finished product possesses certain other disadvantages, e.g., it is less plastic and does not resist heat so well. About 5,000,000 lbs. of urea resin were produced in the U.S. in 1933; the output of the U.K. probably being of the order of a quarter of this amount.

When urea and formalin are heated together no separation of aqueous matter occurs, but the liquid increases in viscosity

alcohol) for the water present. There are many other methods, e.g., a solution of urea or a derivative of urea especially dimethylol urea in an organic solvent may be condensed with formaldehyde in the same or another organic solvent to give a resin which may be precipitated or dispersed.

Whatever the process adopted, the broad outline is very similar to that described under phenol formaldehyde, save that sulphite pulp is usually employed as the filler which results in translucent products.

A ball mill consisting of a large cylindrical container rotating on its longitudinal axis, and quarter filled with marble balls, is used for finally incorporating the resin and filler. This results in the compacting of what would otherwise be a very bulky, fluffy powder.

The moulded articles are familiar to the public under the name of Beatl ware. The moulding powder is more bulky and more difficult to tablet, while stainless steel moulds must be employed to prevent staining of the tool by the moulding compound.

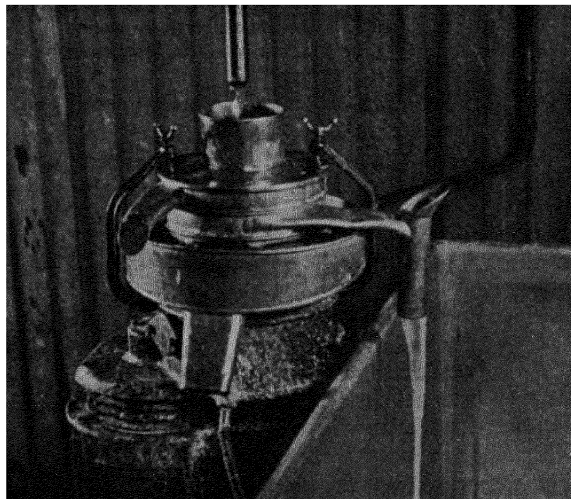


Fig. 1.—MANUFACTURE OF BEETLE MOULDING POWDER (1).

The resin is clarified by means of a centrifuge.

and the resin formed remains dispersed throughout as a sol. The second stage is a transformation from the fluid sol state to the rigid gel condition. The third stage occurs by the expulsion of water from the interior (synerises). Finally, on continued heating, a useless amorphous mass eventually remains which is without lustre and full of large fissures.

Methods of Obtaining a Resin Free from Moisture.

In order to obtain a resin free from moisture and uncombined formaldehyde, the hydrosol may be changed by substituting an organic solvent (e.g., benzyl

Mixed Phenol and Urea Resins.

The technical manipulation is more difficult and, therefore, in order to overcome some of these difficulties part of the urea is often replaced by phenol. The mixed condensation product of phenol formaldehyde and urea when the reaction is carried out by refluxing and then dehydrating in vacuo yields a resin which is soluble in methylated

spirit giving stoving lacquers superior to straight phenol formaldehyde resins, both as regards adhesion and light fastness.

Synthetic Unbreakable Glass.

Synthetic unbreakable glass is made by reacting upon urea or thiourea $\text{CS}(\text{NH}_2)_2$ with formaldehyde under extremely carefully controlled conditions. Warping of the finished product nearly always occurs.

Glycerol-Phthalic Anhydride Resins (Glyptal Resins).

There is yet another type of resin which is rapidly assuming great importance,

viz., that produced by reacting on a polybasic acid with a polyhydric alcohol. The acid usually selected is phthalic acid which has recently been produced in commercial quantities by the catalytic oxidation of naphthalene from coal tar, while the alcohol adopted is glycerine

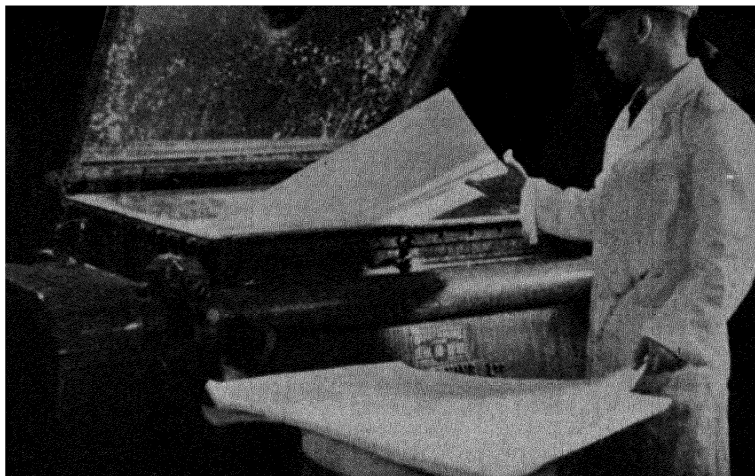


Fig 2—MANUFACTURE OF BEEBLE MOULDING POWDER (2).
Adding cellulose pulp to a mixer containing the resin

How Produced.

The resin itself is extremely easy to produce by heating together, for example, three parts of phthalic anhydride with two parts of glycerine and half a part of oleic acid as catalyst. Three stages in the condensation may be distinguished with some little difficulty. Even in the final stage the resin remains in a more or less rubbery condition.

Uses.

It is used as a cement for building up mica sheets from small fragments, replacing shellac for the purpose, as it adheres tenaciously to smooth surfaces.

It is not soluble in oils, but by adding drying oils and fatty acids during the manufacture together with a carrier to take the resin into the oil, very efficient paint media may be obtained which have extraordinarily high gloss, great tenacity and comparatively good

fastness to light. The development of these resins lies largely in the paint and varnish industry, to which section reference should be made.

Predicting the Properties of a Synthetic Resin.

R. H. Keinle, as a result of work on phthalic acid resins, put forward three postulates which may be used to predict the properties of a synthetic resin formed from any given raw materials. Certain

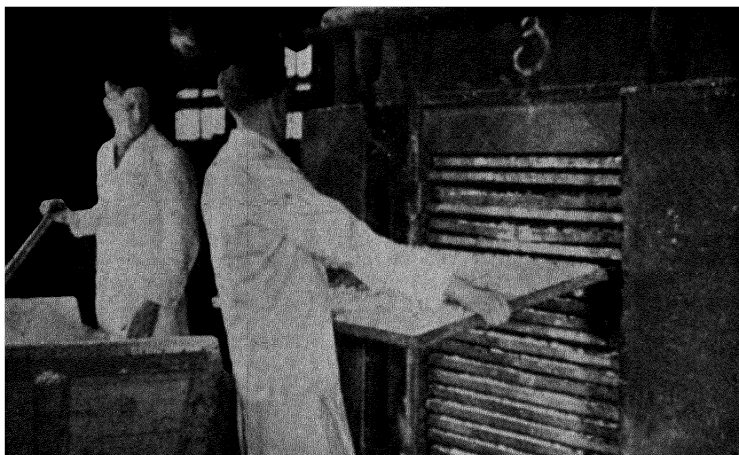


Fig 3—MANUFACTURE OF BEEBLE MOULDING POWDER (3)
The resin having been thoroughly digested with the cellulose pulp in the mixer, is taken out and placed on trays, which are inserted in a drying oven as shown above.



Fig. 4.—MANUFACTURE OF BEETLE MOULDING POWDER (4).

The mixture is then ground to a fine powder in a ball mill. Here we see the mill being unloaded.

anomalies inexplicable by the theory exist however.

Behaviour of Polyreactive Substances.

The first postulate states that organic compounds of high molecular weight are only formed in polymerisation reactions when the interacting substances are polyreactive. In other words, it is possible to say whether a reaction product of two simple substances will be a third definite substance or an ill-defined body of high and indefinite molecular weight, i.e., a resin. The postulate, it will be observed, states that for the latter condition to occur, the molecules of the reacting substances must each have more than one primary reactive valency bond taking part in the reaction.

Glycerine, for example, has three potentially reactive hydroxyl groups, each of which can behave as a base and react with acids to form esters. A simple monobasic saturated acid with only one reactive group, e.g., benzoic, forms with glycerine a definite ester of known characteristics. Such an action is termed 1-3. Polybasic acids on the other hand, such as phthalic acid with two reactive groups or citric with three, give resinous (indefinite)

compounds. These reactions are described as 2-3 and 3-3, respectively.

Reaction of any Two Molecules.

The second postulate states that the reaction of any two molecules proceeds by the fortuitous contact of two reactive points. Chance determines whether a given reactive group of the first substance touches and reacts with any of the reactive groups of the second substance and, therefore, the resulting molecules of the reaction are of assorted sizes. This enables the prediction to be made that resin forming reactions of *this kind* will be rapid at first when the possible number of contacts is large and slow towards the end with increased viscosity due to large molecules which are not mobile.

Theory of Formation of Fusible and Infusible Resins.

When the two reactive agents are both directive only long chain molecules are formed, and such reactions are characterised by continuous increase in viscosity, without ever reaching a condition of infusibility. These 2-2 type reactions give permanently fusible resins; i.e., they are non-heat reactive. If one (or both)



Fig. 5.—MANUFACTURE OF BEETLE MOULDING POWDER (5).

The powder discharged from the ball mill is sieved through silk screens as shown above.

of the initial reacting materials has a reactivity greater than two, the number of possible molecular combinations at once becomes much greater and the final molecules can grow in ways other than that of a straight chain, and can lead eventually to inert infusible and insoluble products.

Heat and Oxygen Convertible Resins.

The potentially reactive bakelite resins are convertible to this stage by heat alone, but the action of a third substance is necessary to convert, for instance, drying oils or rubber to this condition. When a paint film dries by the action of the di-reactive oxygen of the air combining with the tri-reactive glycerides contained in the oil, the reaction is of the 2-3 type.

The chemist can thus predict which substances will form resins of a permanently fusible nature and which will form resins of the heat or element convertible type. The latter are usually more useful.

Relative Shape and Size of Molecules.

Postulate No. 3 states that the relative size and shape of the molecules resulting from an organic reaction largely determine the physical properties of the polymers and enables the chemist to state which substances must be chosen to obtain a resin of the required hardness, water-resistance, flexibility and softening point, from a knowledge of the molecular structure.

The physical properties such as those enumerated are influenced by the number and nature of the reactive bonds. A tri-reactive body (e.g., glycerine) can produce a very flexible resin by coupling with a dibasic acid in which the acid (COOH) groups are separated by a long molecular chain, e.g., succinic acid $\text{COOH} \cdot \text{CH}_2 \cdot (\text{CH}_2)_4 \cdot \text{COOH}$. When the number of potentially reactive bonds increases the hardness of the resulting

resin increases, e.g., tribasic citric acid gives a hard glossy resin. Double bonds, e.g., maleic acid, produce tough resins.

An excessive number of OH groups, e.g., the reaction of phthalic acid and manitol, gives a resin of bad water resistance owing to some of the OH groups remaining unreacted and forming points for attachment of water molecules.

CUMARONE RESIN.

It is estimated that about 60,000 tons of cumarone resins are produced annually in the world, so from the point of view of production this type of synthetic resin is probably the most important of all, although not produced in England owing to patent restrictions. Because its uses are not spectacular it is almost unknown save to technical experts. The neutral solvent naphtha fraction of coal tar which boils at 160-225° C., i.e., that fraction which lies between the light and heavy benzoles, contains the unsaturated hydrocarbons known as cumarone, indene, styrol and cyclopentadiene (the first two being the most important), and

these compounds polymerise fairly readily by contact with concentrated sulphuric acid to give a series of resins known as cumarone resins, which vary according to the conditions of preparation.

Properties of Cumarone.

Cumarone is an oily water-white liquid with a boiling point of 172° C. It yields a resin on treatment with bleaching powder or potassium permanganate, i.e., by oxidation. By polymerisation using sulphuric acid or aluminium chloride, para-cumarone is produced. An excess of acid tends towards the formation of infusible and insoluble compounds which on account of defects, such as brittleness, are not so useful as the soluble and fusible



Fig 6 - MANUFACTURE OF BEETLE MOULDING POWDER (6)

The powder is then packed into tins ready for dispatch. The tins are carefully cleaned inside and out with a vacuum cleaner before handling to avoid possible contamination.

resin produced as explained below. Indene is very like cumarone, boiling at 10° C. higher. Air oxidises indene to cumarone at the same time some resinous matter is thrown down. These facts were known in 1890, as were the main manufacturing details for the production of cumarone resins. Crude solvent naphtha is washed first with soda then with dilute sulphuric acid. It is then treated at 110 - 120° C. with 5 per cent. of its volume of 60° Bé. sulphuric acid.

Resinification occurs on refluxing and the resin remains behind after distillation. At least 40 different grades of cumarone resin are obtainable on the market, varying from soft plastic masses to resins with a melting point of 140° C.

Tests on Cumarone Resins.

The technical examination of these resins is a matter of some difficulty. Generally, the most important characteristics are melting point, mineral matter, acidity and insoluble matter.

Melting Point.

The melting point, in common with all resinous substances, is indefinite and varies with the method of test. The ordinary capillary tube method noting both the temperature of initial sintering when the sharp edges begin to round off and the stage of complete fluidity is probably as satisfactory as any. An American method consists in immersing a standard cube in mercury which is gradually heated till the resin melts and rises to the surface.

The mineral matter (ash) should not exceed 5 per cent.

Acidity.

The acidity is mainly due to residual traces of sulphuric acid which are difficult to remove. A neutral sample will often develop acidity in, say, benzene solution on standing for a few days. The acidity may be determined by extracting the benzene solution with hot water and precipitating the soluble sulphate as barium sulphate by means of barium chloride. The test should be completely negative if the resin is to be used in varnish.

Insoluble Matter.

Insoluble matter may be determined

by dissolving 3 gms. of the sample in 15 c.c. of ether and cooling in ice water. 45 c.c. of 96 per cent. alcohol are added and the solution is allowed to stand for half an hour, filtered and washed with 15 c.c. of ice-cold 96 per cent. alcohol. The soluble matter is obtained by evaporating and weighing the filtrate. The residue is treated with acetone and the insoluble matter, consisting of asphaltic substances, weighed. Examined by this method the percentage of matter soluble in acetone and insoluble in ether mixture varies with the hardness.

The hardest resins contain from 52-53 per cent. insoluble, while the softer contain from 5-7 per cent. Cumarone resins when very dark may be distinguished from coal tar pitches by their solubility in acetone.

Uses of Cumarone Resins.

The various grades of cumarone resins are used as constituents of chewing gum, of printing ink, of varnishes and of oil cloth, as well as in the electrical industry. They resist alkalis and are sometimes used in moulding compositions. The special function of cumarone resin in varnish is dealt with in detail on page 974. Cumarone resin is identified by diluting 1 c.c. of a 10 per cent. solution of the resin in chloroform with 6 c.c. of chloroform and 1 c.c. glacial acetic acid. The solution is shaken and 1 c.c. of a 10 per cent. solution of bromine in chloroform added, the solution again shaken and allowed to stand. The presence of cumarone is indicated by a permanent red colour. Pontianic resin if present imparts a yellow colour. Confirmation is obtained by distilling, recovering cumarone and indene and identifying their picrates.

Other Resins.

Furfuraldehyde or furfural condenses with formaldehyde to give dark resins useful as wood stains and as modifying agents for phenol moulding powders. It also reacts with ketones and amines and alkalis to produce resins with technical possibilities.

Vinyl Resins.

The group $\text{CH}_2=\text{CH}$ —known as vinyl—is derived from the group ethylene C_2H_4 . Most of the vinyl compounds

polymerise readily, especially on exposure to light. The acetate is usually employed and a Canadian company is manufacturing the resins commercially. They are clear and very pale and an immense amount of scientific work has been done on the subject.

Acetone Resins.

These are typified by acetone-formaldehyde resins. They are very pale and flexible and may be used in varnishes, though their resistance to water is very poor.

Procedure with New Resins.

When a new resin is made in the laboratory, the cost under manufacturing conditions should be worked out as exactly as possible, and the following should be carried out in order to determine its chief characteristics to see if it be likely to prove of outstanding merit in any particular direction not covered by existing products.

General Tests.—(a) Melting point and acid value; (b) behaviour under heat, including charring tests and inflammability; (c) discoloration on exposure to light, especially ultra-violet light; (d) solubility in various solvents including alcohols, ketones, hydrocarbons; (e) solubility in drying oils; (f) nature of the film obtained from (d) and (e). This will indicate its suitability for lacquers or varnishes; (g) general electrical properties; (h) compatibility with fillers; (j) moulding characteristics; (k) machining characteristics both with and without fillers; (l) water absorption; (m) resistance to acids and alkalies; (n) adhesive qualities. This should indicate if it be more suited for a varnish material or a moulding material. The following detailed tests are then performed:—

As a Lacquer Constituent.

Determine how the resin solution behaves under the brush. It should not "string out."

Determine how quickly the coat dries and whether any solvent is retained. The film should dry hard and should bear sandpapering. Examine its compatibility with cellulose derivatives, e.g., the nitrate and various plasticisers, e.g., castor oil, tricresyl phosphate, as well as with shellac and other typical resins. Note the elasticity of the film from

various solvents and mixed solvents, by painting on tin and bending. This will also indicate adhesion.

As a Constituent of Oil Varnishes and Enamel Paints.

Note the temperature at which solution commences in linseed oil, tung oil and stand oil, and if darkening is severe when the mixture is raised to 650° F., see if precipitation occurs on adding common diluents like white spirit. A dilution ratio of 2 to 1 should not lead to cloudiness.

Examine the drying time for various oil lengths and note if adsorption of particular drying metals occurs, e.g., xylene resins will not dry at all, unless special steps are taken. Note whether yellowing of the film occurs under several different kinds of conditions, e.g., moist air, ultra-violet light, in total darkness, etc. Test the adhesion to various surfaces and note the interval between which two coats may be applied without "picking up" of the under coat. Weathering tests under various conditions in different parts of the country should be performed in comparison with a varnish or paint of known behaviour as standard. The water resistance of the film should be determined, the contact angle against water being of particular value. The gloss, and hardness of the varnish film with various oils and oil lengths should be ascertained. The toughness of the varnish film may be estimated by the Kauri reduction test (see page 975). It goes without saying that the working properties should be good, that is, there should be no pull under the brush and the varnish should flow out readily to a smooth even film. No webbing or frosting should occur during drying in an atmosphere saturated with the products of combustion of coal gas or kerosene. If an insulating varnish is being examined, further tests for impregnation and electrical properties are necessary.

As a Constituent of Moulding Powders.

Good wetting of the filler is desirable or sticking to the mould by the uncoated fibres is liable to occur, leading to surface scratching of the tool and spoilt articles. The compression ratio, i.e., the volume of powder compared with the volume of the finished article, should not be too high, certainly not greater than three to one.

It is also better if tablets can be produced by a single stamping operation rather than by a gradual compressing process in a rotary head machine.

Staining of the mould should not occur, nor blistering of the moulded article. Shrinkage should not be too great. A slight amount is desirable in order to secure ready removal of the article from the moulding tool.

The moulding temperature range of the powder should be determined. It is preferable that this should not be too narrow as temperature fluctuations are always liable to occur on press platens. Malodorous vapours should not be evolved during the pressing operation and the articles should not warp on removal from the hot mould.

Tests on Finished Moulding.

The finished moulding should be submitted to the following tests in the new condition and, in the case of electrical tests, after immersion in water, salt water, moist air, sulphuric acid, and transformer oil under specified conditions for periods of one week. The specific insulation resistance should be determined and expressed as megohms per centimetre cube as well as the surface resistivity or surface leakage and the electric strength or breakdown voltage. It is also important to determine when arcing occurs on the surface whether the latter becomes car-

bonised and conducting or whether it still retains some of its insulating qualities.

Mechanical Tests.

The mechanical tests include toughness, performed on an impact test machine, cross-break strength, plastic yield with temperature (rigidity) and crushing strength. An artificial ageing test may be carried out by testing the material before and after exposure to moderately high temperature for specified periods. The water absorption of the specimen may be ascertained by a separate test, though this will be revealed by the electrical tests carried out after immersion.

Machining and Tooling Characteristics.

Lastly, the machining or tooling characteristics are measured by taking four helical cuts on a rod of the material and measuring the tool wear.

As indicated at the beginning of this section (page 717) the number of possible resinifying reactions is infinite. Certain resins with extremely valuable properties are not available commercially owing to the high cost of the raw materials. At any time, however, these raw materials may suddenly greatly decrease in price, due to new methods of manufacture. The resin is then marketed and so development proceeds and yet another material is available to add to the worries of technologists.

POISON HAZARDS IN INDUSTRY

By SIDNEY L. TOMPSETT, Ph.D.(Gles.), I.Sc.(Lond.), A.I.C.

THE modern works manager should be familiar with industrial diseases as to their cause and prevention, as compensation in such cases must form a considerable part of the works costs in many instances.

An intricate knowledge of medicine is not demanded, as in these days much of modern medicine may be interpreted in terms of chemistry and physics, in fact the modern physician is looking to the chemist and the physicist for a solution of his many problems.

Toxic substances can gain entrance to the body by three routes:—

(1) Absorption from the intestine as the result of taking the substance in question in with the food, etc.

(2) Absorption through the skin as a result of handling.

(3) The inhalation along with dust and consequent absorption in the lungs.

Most people are familiar with the first route but the others are usually lost sight of. These latter two routes of entrance to the body often produce the most serious conditions.

THE METALS.

Copper.

This metal is a constant constituent of all tissues, both human and animal. The following figures represent the distribution of this element in normal human tissues:—

Liver	4-10	} mg. per kilo. (fresh material).
Kidney	2-4	
Brain	2-4	
Spleen	1-2	
Pancreas	1-2	
Bone (rib)	4-15	
Bone (vertebra)	2-4	
Blood	0.18-0.23	mg. per 100 ml.

An average daily diet contains 1.5 to 2.5 mg. Cu, while 1.8 to 2.2 mg. are excreted daily in the fæces and 0.2 to 0.4 mg. in the urine. It has now been definitely shown that copper is a necessary element in the body and although not a component,

is concerned in the formation of hæmoglobin for the red blood cells.

In some conditions the concentration of copper in the tissues may be increased without any abnormal exposure to the element.

In cirrhosis of the liver, the liver often contains a high concentration of copper, figures up to 114 mg. per kilo (fresh material) having been obtained. In hæmochromatosis, a rare condition, results similar to those obtained in cirrhosis of the liver have been recorded.

Quite large amounts of copper can be tolerated; in fact, copper sulphate is often given along with iron in the treatment of certain anæmias. Copper salts in excessive amounts are violent gastro-intestinal irritants, so that after a big dose the greater portion is removed by vomiting.

Industrial diseases ascribed to copper have been described, but these have usually occurred in conjunction with the use of other metals, e.g., arsenic, lead, antimony, and it is most likely that the symptoms are due to these and not to copper.

Manganese.

This element is a constant constituent of the tissues, natural foodstuffs, and the excreta of the human and the animal. The distribution in the normal human body is shown in the table:—

Liver	4 mg. per kilo fresh material.
Kidney	1.5 mg. per kilo fresh material.
Urine	About 0.02 mg. per day.
Fæces	4-6 mg. per day.
Blood	About 0.02 mg. per 100 ml.

The average daily diet contains about 4-6 mg. of manganese.

It has been suggested that manganese is necessary and essential for reproduction. It plays no rôle as copper does in the formation of blood.

In industry, symptoms have been ascribed to the inhalation of the dust of

the metal and its compounds. These are emotional symptoms, muscular weakness, etc.

Mercury.

This is not a normal constituent of the body. Mercury poisoning in industry occurs mainly from the vapour of the metal, which is given off at mean temperatures and freely in the warmth. It is absorbed from the respiratory and digestive tracts and through the skin. The symptoms are anæmia, timidity, excessive salivation, etc. In severe cases of mercury poisoning, the kidneys may be damaged. In this condition the secretion of urine is inhibited and the blood urea may be as high as 100-300 mg. per 100 ml.

As a preventive, the air in a work-room using metallic mercury should be below 90° F. and all spilt mercury gathered up.

Aluminium.

This metal is a constant constituent of natural foodstuffs, and therefore of the tissues and excreta. This is to be expected since aluminium forms a large part of soil.

On an average, the daily human diet contains about 12 mg. of aluminium, of which at least half comes from the food and not from the cooking vessels.

In the past few years, gastric symptoms ascribed to the use of aluminium cooking vessels have been described. Undoubtedly all such symptoms are purely psychological.

Zinc.

This metal is a constant constituent of normal tissues and of the daily diet. The table illustrates its distribution.

Liver about ..	50	} mg. per kilo. (fresh material)
Kidney about ..	30	
Bone about ..	100	
Brain ..	10	

Blood about 1 mg. per 100 ml.

Urine about 1 mg. per day.

Fæces about 10 mg. per day.

Average daily diet, 10-15 mg.

It will be noticed that this element tends to accumulate in the bones. Whether or not it has any definite physiological action has not been shown.

In industry a condition known as "brassfounder's ague" has been described. The attacks resemble a malarial chill and are accompanied by headache, lassitude, cramp, joint pains, etc. It is

caused by the inhalation of dust containing metallic zinc or its oxide.

Lead.

Undoubtedly this metal and its compounds form one of the greatest hazards in industry. Lead in small amounts is a constant constituent of human tissues and the diet and excreta.

The normal :—

	mg. per kilo.
Liver	1-2
Kidney	1-2
Brain	0.2-0.5
Bone (rib and vertebra)	6-12
	mg. per diem.
Urine	0.01-0.15
Fæces	0.1-0.5
Diet	0.1-0.6

Lead has an intensively cumulative action and appears to collect in the bones. This is true for the normal and for those exposed to excessive amounts of lead. In industry the two most important sites of absorption are the respiratory and digestive tracts. Of the two, the former is the most dangerous, since the lead will be absorbed directly into the circulation. In the latter case, lead that is absorbed is picked up by the portal vein, carried to the liver which can excrete some at least, back into the intestine before it can reach the general circulation.

In industry, lead poisoning is caused mostly by inhalation of lead-containing dust. Many measures, e.g., exhaust ventilation, damping down of dust, have been adopted, but cases of lead poisoning are still very common. Lead poisoning is common amongst shipbreakers, due to the volatilisation of lead paint by the heat of the oxy-acetylene flames. Painters should, strictly speaking, not develop lead poisoning if they are clean in their habits.

Forms of Lead Poisoning.

Lead poisoning may manifest itself in a variety of ways.

(1) Lead colic.—This appears as persistent constipation and abdominal pains.

(2) Muscular paralysis, e.g. wrist drop.

(3) A marked anæmia. When this is present the cells show stippling which is characteristic of lead poisoning.

(4) Kidney damage.—Often the kidney is damaged and sometimes permanently. The blood urea may sometimes reach the high levels of 100-300 mg. per 100 ml.

(5) Cerebral symptoms—these are rare.

Even in lead poisoning most of the metal is to be found in the bones. Lead in the bones is in a non-toxic form. Only that lead present in the other tissues and the circulation exerts toxicity.

The following figures are the analyses of the bones and tissues of lead workers who apparently did not suffer or die of lead poisoning. Naturally the question might arise as to what part lead did play in bringing on the condition they died from. This is difficult to assess.

	mg. per kilo. (fresh material).		
	Painter.	Paint Works' Operative.	Painter.
Liver	.. 5.74	5.6	4.5
Kidney	.. 0.54	1.08	1.0
Brain	.. 0.7	—	1.0
Bone (rib)	.. 44.8	53.0	119.4
Bone (vertebra)	43.8	—	18.8

Prevention of Lead Poisoning.

The prevention of lead poisoning has been attacked from an entirely different angle within recent years. It has been previously stated that lead in the bones is not toxic, so that if lead absorbed by a lead worker could be fixed in the bones, lead poisoning should not develop. The presence of a large amount of calcium in the diet is extremely favourable for this process to take place. In many industries this preventive measure is taken and milk being the richest source and the cheapest, is given for this purpose. It may be mentioned that the calcium in milk is the most easily assimilable form known.

A lead worker on a high calcium diet may show no signs of lead poisoning, but if he changes to a very low calcium diet, symptoms may begin to show even although he may have been removed from the source of exposure for some time. This is because a low calcium diet is favourable to the passage of lead from the bones into the circulation and tissues, i.e., the reverse to the above.

Diagnosis of Lead Poisoning.

The chemist is often called in to assist in the diagnosis of lead poisoning. In such cases the urine and *fæces* should be analysed quantitatively for lead, at least three-day collections being used. The chemical findings only go to show whether an excessive excretion of lead is present.

They do not represent a diagnosis. Sometimes a man exposed to lead in industry may show typical signs of lead poisoning yet his excretion of the metal may not be excessive. On the other hand, a perfectly healthy worker may be found to be excreting quite large amounts of lead.

Similarly, analyses of tissues post-mortem can only be used in conjunction with the findings of the pathologist. At the present time the writer has developed a method for estimating the lead content of blood and is attempting to correlate this with the general symptoms.

Lead is excreted mainly in the *fæces* so that this material should always be examined along with the urine.

Another difficulty in the diagnosis of lead poisoning from chemical analysis is that the workman who has been away from exposure gradually excretes less and less lead until his excretion may be only slightly above normal. This does not represent that the lead content of his tissues and bones have dropped to normal.

Arsenic.

This element occurs in minute amounts in human tissues, and some suggest that in these concentrations it exerts an essential physiological action.

Arsenic was, a few years ago, a popular method for murder. In chronic arsenical poisoning, the symptoms are, eczema, ulceration, and pigmentation of the skin, gastric derangement, anæmia. There is a risk from chronic arsenic poisoning in the smelting of native sulphides, in the fur trade, where it is used as a preservative, in tan yards, and in the preparation of sheep dips.

The gas arsine is extremely poisonous and may be freed in dangerous amounts in works where acids, e.g., sulphuric acid, hydrochloric acid act on metals such as iron, tin or zinc, since arsenic is a common impurity of any of these materials. Arsine is also liable to be produced along with phosphine, another very poisonous gas, when water comes in contact with ferro-silicon. A severe jaundice is the typical symptom.

Antimony.

This metal is not a normal constituent of the body, although large amounts may be found in the *fæces* of workers using it, it does not appear to be an industrial hazard.

Radioactive Metals.

These and the X-rays may be classed together since both evolve α , β and γ rays. The former are not really rays but actually particles of matter. The α rays are the most destructive agents known to science and are 10,000 times more destructive than the γ rays. They, however, may be effectively screened owing to their poor penetrating power.

Industrial disease has arisen in many instances by the entrance to the body of radioactive material. Although the amounts assimilated may be infinitesimal, they tend to be stored in the bones and are thus cumulative. Such conditions have arisen in workers amongst radioactive materials and girls employed in painting the luminous dials of watches, etc. In the latter class of worker the trouble appears to have arisen through the habit of repeatedly licking the tips of their brushes. Being stored in the bones, the bone marrow is under a continual bombardment of α rays. Owing to the low penetrative power of these rays, the bone marrow is destroyed and an anæmia develops. This is due to the fact that the bone marrow is the seat of the formation of the red blood cells. In addition, the lower and upper jaws develop lesions due, as in the case of phosphorus poisoning, to a bacterial infection superimposed on a destruction of bone.

Once the α particles are deposited in the bone they cannot be removed. Similar fatal cases have been reported from America through drinking large amounts of radioactive waters.

PHOSPHORUS.

Yellow phosphorus, owing to its volatility is extremely dangerous to use, and when it was used in the match industry was a big hazard. With the substitution of red phosphorus in this particular industry, this has disappeared. The hazard still persists in the preparation of the element and in the manufacture of phosphor bronze. The poisonous action of yellow phosphorus is due to the inhalation of the vapour. It is a powerful liver poison, jaundice being produced. Its typical symptom is the so-called "phossy jaw." This is due to a destruction of the jawbones, upon which is superimposed a bacterial infection.

Phosphine is extremely poisonous, 0.2

per cent. in the air being quickly fatal. Industrial poisoning arises from its presence sometimes in acetylene and by the action of water on ferrosilicon (see arsine).

SILICA, ASBESTOS, COAL DUST.

The long continued inhalation of certain irritating dusts produces a condition known as pneumoconiosis, which is accompanied by persistent and irritating coughing. The presence and amount of silica is the determining factor in the outcome of such a condition. Silicosis and asbestosis usually prove fatal, whereas anthracosis is comparatively harmless.

Silicosis.

This is the most common and the most important of the dust diseases and proves a serious problem in certain gold-mining districts, e.g., the South African Rand. Sometimes in coal-mining hard rock has to be bored, e.g., the South Wales coalfield, so that coalminers may suffer from such a condition. It may occur in tin-mining, stone working, metal grinding and sand blasting.

The condition is due to the inhalation of fine particles of silica. They are sharp-edged and are deposited in the lung tissue. Silica is slightly soluble and can thus have a definite chemical action. Silica "kills" the neighbouring cells, producing what is known as a necrosis. The majority of silicotics die of tuberculosis as silica appears to favour markedly the growth of the tubercle bacillus in the lungs.

In life, the condition is best diagnosed by an X-ray examination of the chest.

Asbestosis.

This condition is very similar to the previous and is due to the inhalation of asbestos dust, which may contain up to 50 per cent. of silica. It occurs in those occupations involving the crushing of asbestos rock and in the carding of the asbestos.

Anthracosis.

This is caused by the inhalation of coal dust. It causes little irritation as the particles of carbon are insoluble. It has no predisposition to tuberculosis.

ORGANIC SUBSTANCES.**Aniline.**

Poisoning often occurs in those associated

in the manufacture and use of this substance. Absorption takes place through the skin. In acute cases there is pallor, with cyanosis, due to formation of methæmoglobin in blood. As has been mentioned previously, methæmoglobin, although containing oxygen, is a poor respiratory pigment owing to its strong combination with oxygen, i.e., it is unable to give up its oxygen readily to the tissues. In chronic cases, i.e., absorption of small amounts over long periods, other symptoms, such as eczema and papilloma of the bladder occur. Papilloma is the formation of numerous wart-like bodies over the surface of the bladder. It is not a malignant condition, i.e., not a cancer, but may develop into such. Sometimes these growths bleed, and blood containing oxyhæmoglobin and methæmoglobin may be found in the urine.

Benzene.

In acute cases of poisoning it acts by direct irritation of the nervous system, producing excitement, followed by coma. In chronic cases there is usually an anæmia.

Toluene and xylene, on the other hand, do not appear to be industrial hazards.

Nitrobenzene.

The symptoms of poisoning by this substance are very similar to those of aniline. Chronic poisoning is usually associated with a marked anæmia, due to a destruction of the red blood cells. Sometimes a jaundice develops.

Trinitrotoluene, Picric Acid, Tetrachloroethane, Dinitrophenol.

These are very powerful liver poisons. Poisoning by these substances is associated with an anæmia due to destruction of the red blood cells, and in some cases with a very marked jaundice.

Carbon Tetrachloride.

Apart from producing unconsciousness, it has a powerful toxic action on the liver, producing a jaundice.

DERMATITIS.

Dermatitis may be defined as an inflammation of the skin and can make its appearance in a variety of ways, depending on the nature of the irritant. The area of skin inflamed may be affected

uniformly or only in patches. In some cases blisters may form. If these are small they are known as vesicles, and if large, as bullæ. These may burst and either form an ulcerating surface or dry up and form a scab or crust.

Dermatitis is caused by irritants and is probably one of the greatest of industrial hazards since there is probably not an industry immune from it. In cases of industrial dermatitis, an attempt should always be made to determine the nature of the irritant, especially in isolated cases, as dermatitis can quite often be produced by irritants used in ordinary domestic life.

Causes of Dermatitis.

There are so many substances of use in industry which have been considered as causatives of this condition that it is almost easier to state those that do not. Probably the most important causatives are the alkalis, the acids, chrome salts, turpentine, formaldehyde, the tars, mineral oils, sugar, dough, and dyestuffs and intermediates. It should always be borne in mind that many of the substances used by operatives in cleansing the hands are themselves provocative of dermatitis, e.g., soda ash, turpentine, paraffin, methylated spirits.

The condition may arise from the handling of certain plants. Poison ivy (*Rhus toxicodendron*) produces very marked symptoms, and although this species is rare in this country, Japanese lacquer, which is made from one of the species of the *Rhus* family, may give rise to symptoms in a susceptible person. Dermatitis may be produced by handling *Primula obconica*, *Daphne mezereum*, parsnip, daffodil and chrysanthemum. The handling of such woods as teak, ebony and satin-wood sometimes produces a dermatitis.

Certain substances used for medicinal purposes are provocative of dermatitis, e.g., cantharides, croton oil, chrysarobin, iodine, etc.

Cases of dermatitis have arisen by the use of certain hair dyes, especially those containing *p*-phenylene diamine. Similarly, the use of cheap furs which have been dyed by the use of *p*-phenylene diamine, etc., have produced dermatitis.

Dermatitis is not uncommon in those of none too cleanly habits. This is produced by the decomposition of excretions such as sweat, etc.

Dermatitis which occurs in some industries if not attended to may develop into a malignant condition such as a cancer of the skin. This is especially true of those associated with coal tars, certain mineral oils, shale oil, etc.

In addition to the above, french polishers, photographers, leather workers, grocers (sugar), are liable to dermatitis through handling substances used in their trades.

Susceptibility to Dermatitis.

The peculiar thing about dermatitis is that when an outbreak occurs in a factory, all are not affected. This opens the question of susceptibility. The susceptibility towards a particular substance varies considerably amongst individuals. Also it will be noticed that a dermatitis does not develop immediately on coming in contact with an irritant, but a period of time always elapses. It is considered that during this period sensitivity towards the substance is being developed.

It is important, when an outbreak occurs, to determine the cause, with a view to prevention. Although it may not be possible to determine the chemical nature of the irritant yet it is possible to exclude materials in which it is present. It should be remembered that often it is the impurities in substances and not the substances themselves which provoke the dermatitis, e.g., although many oils used for lubrication purposes may be of similar chemical constitution yet only some provoke dermatitis.

Detecting Dermatitis-producing Materials.

The patch test has been particularly useful in detecting dermatitis-producing materials. If the material is soluble in water, the solution is soaked in lint and placed on a sound piece of skin of an *affected* person. The lint is covered with a piece of gutta-percha tissue and the whole covered with a bandage. The forearm, if available, is most suitable for this test. If the person is sensitive to the material, an eruption will appear within 24 hours and the dermatitis is in all probability caused by the material under test. If the skin remains normal the test is negative. If the material is insoluble, a suspension in water is placed on the lint and the test carried out as above. Possibly

it might be required to test such materials as rubber gloves to see whether they have provoked a dermatitis. In such cases a piece of the rubber is moistened and placed on the lint and the test carried out.

Such tests are obviously not carried out with acids, alkalies and chromates since in these cases the action is purely corrosive.

This can only be taken as a very brief outline of dermatitis as the subject is an extensive one, in fact very large books have been written about it.

INDUSTRIAL CANCER.

In certain industries the operatives are extremely liable to a cancerous condition of the skin known as epitheliomatous ulceration. All types of cancer are known as malignant conditions. Non-cancerous tumours, which usually do not recur on removal and do not spread to other tissues of the body, are referred to as non-malignant or benign. Cancerous tumours appearing in one part of the body, e.g., skin, stomach, etc., have a habit of setting up cancerous growths in other parts of the body, especially the liver, even although the first growth may have been removed by surgical methods.

Cancer of the skin is very common in those coming in contact with coal tars, crude petroleum, shale oil, certain mineral oils used in lubrication, etc. Pure petroleum, in contrast to the crude material, does not set up a cancer. Operatives in cotton mills are liable to cancer of the scrotum through the use of certain mineral oils in the frames carrying the spindles. This is often referred to as mule-spinners' cancer. When such conditions do arise, contact is usually over a very long period, i.e., years. The condition does not start in the first place as a cancer but usually as a scab, wart, or dermatitis. It is after this, if no attention is paid, that a cancerous condition arises.

Within recent years evidence has been obtained as to the nature of the cancer-producing substances present in certain coal-tars, etc. These appear to contain the phenanthrene nucleus. Many substances containing the phenanthrene nucleus have been synthesised and have been found to produce a cancer when applied to the skin of animals over long periods. Amongst these may be mentioned benzanthracene, dibenzanthracene, and benzpyrene.

CHEMISTRY IN THE LEATHER INDUSTRY

PART III.—DRYING AND FINISHING LEATHER

By F. E. HUMPHREYS, Ph.D., A.R.C.S., A.I.C.

UP to the end of the actual tanning process all leather, whether light skins or heavy hides, have received fundamentally the same treatment. They have been soaked, limed, unhaired, fleshed and tanned, usually with either vegetable or mineral tanning materials. Having passed through the last tan liquor, however, the treatment which the goods receive varies enormously, according to the use to which they are destined to be put.

Sole Leather.

In order to attain the firmness desired for sole leather it is usual to finish the tannage in strong liquors, the temperatures of which have been raised to about 100° F. Were the leather dried out immediately after this process, it would be of a dark and patchy appearance and too hard and cracky for either the shoe manufacturer or repairer. The leather is therefore "bleached" to even up the colour and remove excess tan from the grain surface. In America this is done by immersing the leather for a short period in a dilute solution of caustic soda, sodium carbonate, borax, or some other alkali, washing in water and dipping in a bath of dilute acid, followed by a final washing in water. This process, however, requires very careful watching, since the hides must remain in the various baths only for a

matter of about half to one minute, or they would be ruined. In this country, therefore, a less drastic, but more easily controlled, process is used. The goods are placed in a pit containing a warm tan liquor, to which a bleach extract, made by autoclaving tanning extracts with sodium bisulphite, has been added and allowed to remain there for from 12 to 24 hours. The leather is then removed, washed in cold water and drained, prior to passing to the drying sheds.

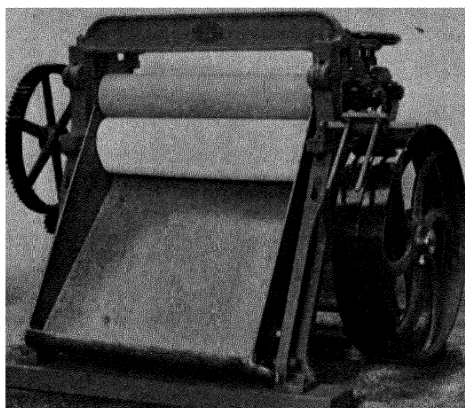
Control of the Bleaching Process.

Even by this latter method, satisfactory bleachings calls for careful control of the bleach liquors. Temperature, an important factor, is, of course, easily measured with a thermometer, whilst the acidity and pH value is best determined by using the glass electrode (see page 918). The sulphur dioxide content of the liquor is determined volumetrically and the amount of sodium absorbed by the leather during the process gravimetrically.

Determination of Sulphur Dioxide.

The total amount of sulphur dioxide or sulphurous acid available in a bleach liquor is determined as follows:—

About 300 ml. of distilled water are placed in a round-bottom flask. To this is added exactly 25 ml. of the bleach liquor under examination



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Fig. 1—SAMMYING MACHINE FOR REMOVING
EXCESS OF MOISTURE FROM HEAVY LEATHER
BEFORE OILING.

and 5 ml. of syrupy phosphoric acid. The flask is then connected to a vertical condenser by means of a splash head and the liquor in the flask heated until it boils vigorously. The distillate is caught in a beaker containing a little water and starch solution, below the surface of which dips the end of the condenser, which is fitted with a trap-bulb to prevent sucking back. During the distillation, standard iodine solution is run into the beaker at such a rate that the blue colour formed by the iodine and the starch is just not destroyed by the sulphur dioxide gas which comes over. The distillation is continued until the blue colour is no longer discharged. Each ml. of N/10 iodine solution is equivalent to 3.2 mg. of SO_2 . The results are expressed as milligrams of sulphur dioxide in 100 ml. of bleach liquor. The "free" sulphur dioxide is determined similarly, but no phosphoric acid is added to the distillation flask.

Uptake of Sodium.

The amount of sodium taken up by the leather is found by determining the sodium content of a sample of the leather before and after the bleaching process.

About two g. of the wet leather is cut into small pieces, after removing any superfluous liquor by blotting with a filter paper, and allowed to dry in the air. It is then placed in a platinum crucible, dried in a steam oven, weighed, ashed, and again weighed. The ash is dissolved in dilute hydrochloric acid and the solution evaporated on a steam bath to about 1 ml.; 10 ml. of a solution of zinc uranyl acetate is then added and the liquor allowed to stand for 30 to 45 minutes, when the precipitate is filtered off through a weighed Gooch crucible, washed with the reagent, alcohol and ether, dried in a vacuum desiccator and weighed. The weight of the precipitate

multiplied by 0.01495 gives the weight of sodium in the material taken.

Shedding.

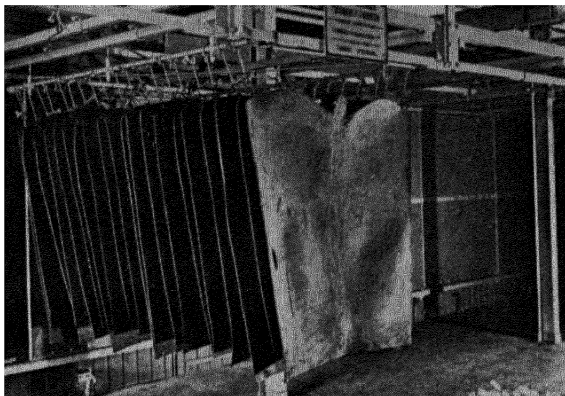
After bleaching, the leather is rinsed in cold water and piled to allow the excess water to drain off. Sometimes it receives a further treatment of glucose and Epsom salts before passing into the drying and finishing sheds. The leather is then "sammied" to a condition suitable for the first oiling, dried to a state suitable for a light rolling or "setting out" and again oiled and further dried before receiving a heavy rolling which compacts the fibres and gives firmness. After further drying, the leather is "stoved" at a temperature of about 90 to 100° F.,

before passing to the warehouse, where it is allowed to "temper back," that is to regain a little of the water lost in the drying stoves, and sorted. The whole of the shedding processes often occupy several weeks and require careful control, particularly with regard to the

moisture content for the various processes. In practice this is usually decided by the feel of the goods, since it would be an impossibility to determine in the laboratory the moisture content of every hide, a procedure which would be necessary on account of the wide individual variation.

Oiling.

Oil is applied to the leather before drying in order to improve the colour and enable it to be firm and yet springy and not cracky. The oils most commonly used for sole leather are mixtures of cod oil, sulphonated castor and cod oils and mineral oils, and must be carefully chosen to suit each individual finishing process. Sometimes the leather is impregnated with a hard grease such as paraffin wax.



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Fig. 2.—A LOAD OF WET BUTTS HUNG READY TO BE PUSHED INTO ONE CHAMBER OF A WILSON DRYER.

Analysis of Oil.

As a general rule oils used in leather manufacture are analysed only to determine the percentage of free fatty acids present, from which we can tell whether or not the oil has become rancid, and the amount of unsaponifiable matter to see whether a large proportion of mineral oil has been added. A rapid test for the presence of mineral oil is to place a drop on a glass slide and examine it with ultra-violet light. The appearance of a brilliant fluorescence indicates the presence of mineral oils. Occasionally it may be necessary to determine in addition the iodine value and such physical properties as the melting or coagulation point, the specific gravity and the viscosity.

Determination of Free Fatty Acid or "Acid Value."

To 50 ml. of 95 per cent. alcohol is added a few drops of phenolphthalein, followed by tenth normal sodium hydroxide, until a very faint pink coloration is obtained. About 2.0 g. of the oil is then weighed out accurately into an Erlenmeyer flask and the neutralised alcohol added.

The mixture is heated to boiling, shaken thoroughly and titrated with tenth normal sodium hydroxide until the pink colour returns and persists even after vigorous shaking. The results are either expressed as the percentage of free fatty acids, calculated as oleic acid, or as the acid value, that is the number of milligrams of potassium hydroxide required to neutralise the free fatty acids from 1 g. of oil.

Determination of Unsaponifiable Matter.

About 3 g. of the oil are weighed accurately into a small flat-bottomed

flask of about 100 ml. capacity and treated with 5 ml. of 50 per cent. sodium hydroxide solution and 45 ml. of alcohol. The flask is then closed with a cork carrying a reflux condenser and heated on a water bath for about 30 minutes, after which the contents are rinsed with hot water into a 1 litre separating funnel. When cool, 100 ml. of light petroleum are added and the contents of the funnel mixed. Care should be taken not to shake too vigorously or an emulsion which is difficult to break may result. When the two layers have separated, the aqueous phase is drawn off into a second separating funnel and

again extracted with petrol. The combined petrol extracts are then repeatedly washed with small quantities of water until the washings no longer react alkaline to phenolphthalein. If emulsions form during washing they may be broken by the addition of a few drops of alcohol. The petrol extract is then filtered through a dry filter into a

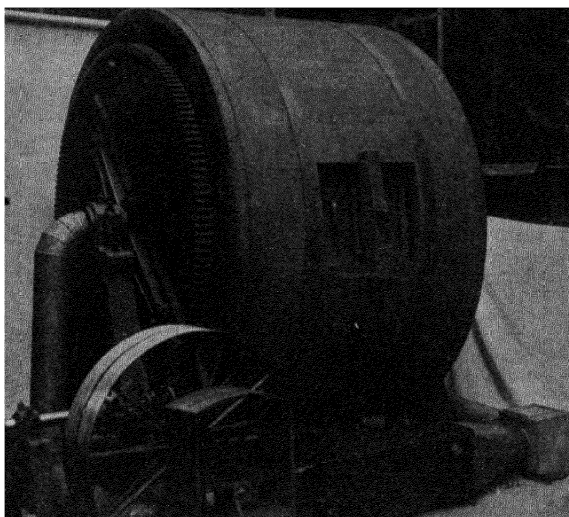
weighed glass crystallising basin and the filter washed three times with small quantities of petrol. The petrol is then evaporated over an electric heater and the dish placed in a steam oven for 30 minutes. It is then transferred to a desiccator and, when cool, weighed.

The results are expressed as the percentage unsaponifiable matter, which equals.

$$\frac{\text{Grams of residue in dish} \times 100}{\text{grams of oil taken.}}$$

Drying.

Formerly the leather drying was accomplished by hanging the wet goods in sheds fitted with adjustable louvres opening into the outside air, the goods being taken down for the various processes



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Fig. 3—A DRUM HEATED BY HOT AIR SUITABLE FOR FAT LIQUORING LIGHT LEATHER.

when the shed foreman decided that their condition was right. Owing to the very changeable climate in this country, however, the modern tendency is to keep these louvres shut and control the temperature and humidity artificially.

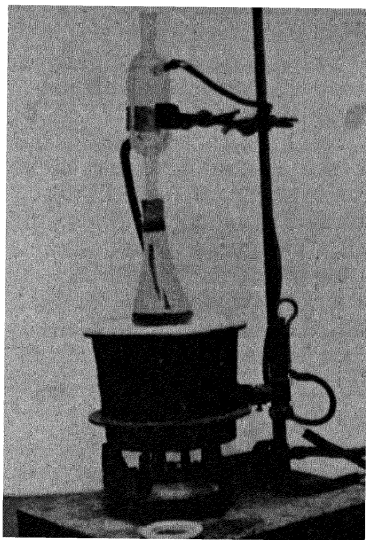
The sheds are usually heated by steam or hot-water pipes, the temperature being read, of course, on a thermometer. The amount of water vapour in the atmosphere, which naturally affects greatly the speed at which the leather will dry, is controlled either by placing on the floor damp sawdust or bowls of water, or by blowing steam, or spraying water into the air.

The ratio of the weight of water vapour in a cubic foot of air compared with the weight of water vapour present, at the same temperature, in a cubic foot of air saturated with water is termed the Relative Humidity of the air and is usually expressed as a percentage.

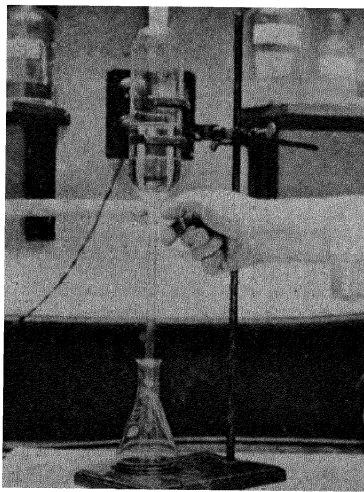
The humidity of an atmosphere can be determined in several ways, but is usually measured, either by means of a wet and dry bulb thermometer or a hair hygrometer or psychrometer.

Wet and Dry Bulb Thermometer.

This apparatus consists of two thermometers, the bulb of one of which is covered with a stocking of muslin or similar material dipping into water. When air passes over the two bulbs the evaporation of water from the wet bulb will cause a lower



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Fig. 4.—REFLUXING AN OIL WITH ALCOHOLIC POTASH TO DETERMINE THE UNSAPONIFIABLE MATTER.



British Leather Manufacturers' Research Assn.
Fig. 5.—SEPARATING THE AQUEOUS AND PETROL PHASES IN THE DETERMINATION OF THE UNSAPONIFIABLE PORTION OF AN OIL.

temperature to be recorded on that thermometer. From a knowledge of these two readings the relative humidity can be calculated or read off from tables. Care must be taken to keep the stocking clean and the water container filled with distilled water.

Hair Hygrometer or Psychrometer.

This instrument makes use of the fact that hair and other fibres alter in length according to the relative humidity of the air. They are almost unaffected by temperature and vary, not with the total moisture content of the atmosphere, but

with the relative humidity. A hair or other fibre is so mounted that any extension or contraction is suitably conveyed to a light needle which moves over a graduated scale. The hair hygrometer is not quite so reliable or accurate as the wet and dry bulb thermometer, but requires less attention and is more convenient where the air flow is very small.

In a number of tanneries to-day drying is carried out in machines in which the temperatures, relative humidity and flow of the air, can be adjusted and are then automatically maintained at the desired levels.

Belting Leather.

Belting leather, or strap butts, do not receive the heavy rolling to which the sole leather is subjected and are usually given only a very light oiling on the grain and then dried right out. The butts

then pass to the currier, who soaks them back and "stuffs" them with a mixture of grease and oil. Two methods are commonly in use for this process, namely, "hand stuffing" and "drum-stuffing." In the former case, after being soaked back and sammied, either the flesh or grain or both sides of the leather are anointed with a dubbin composed of a mixture of tallow and cod oil. The goods are then hung up to dry, after which the "table grease," that is the excess grease on the surface, is scraped off, the leather "set out" and laid away for some two or three months to season.

Drum-Stuffing.

In this method the goods, after soaking and sammying, are placed in drums and heated to about 125°F, the melted dubbin run in, usually through a hollow axle, and the drum rotated for about an hour. The leather is then set out and finished as in hand stuffing.

Light Leather.

The types of light leathers are so varied and the uses so numerous that a large number of finishing processes exist, the majority being, however, mainly mechanical. After tanning, the goods are dyed, fat liquored, set out and dried, usually in a tunnel or a room where warm air is circulated. The next process is known as staking, by which the leather is softened and stretched, followed, if desired, by buffing on the flesh side to give a velvety appearance. The goods are then strained and tacked on to boards, or, in more up-to-date tanneries, fixed to wire frames by means of toggles and again dried. The final process depends largely upon the use to which the leather is to be put and may entail rolling, glazing, ironing, embossing or boarding and print-

ing. Pigments and cellulose finishes are also frequently applied.

Fat Liquoring.

This process is comparable to the oiling of heavy leather and gives the desired "feel" and prevents cracking. In the case of light leather it is usually carried out in a drum, and consists of treatment with a warm emulsion of soap, water, oil, and other substances such as egg-yolk, lecithin, casein and sulphonated oils. The whole of the emulsion is absorbed by the leather and care should be taken that too much oil is not used or the goods will be too soft and greasy to finish satis-

factorily. Also no excess alkali should be present. The egg-yolk, lecithin, casein and sulphonated oils act as emulsifying agents. The leather is then rinsed in hot-water to clear the grain so that the dye will go on evenly.

Analysis of Sulphonated Oils.

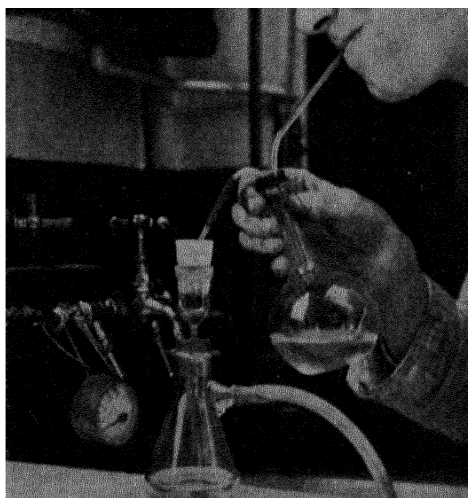
Sulphonated or, more strictly, sulphated oils, are prepared by treating an oil with a strong solution of sulphuric acid followed by washing and neutralisation.

Determining the composition of a

sulphated oil is very complicated, but it is rarely necessary to undertake the complete analysis, certain tests usually being sufficient.

Test for Sulphonated Oil.

A few drops of glacial acetic acid are added to about 4 g. of the oil to render it distinctly acid to litmus, a procedure which greatly facilitates the following separation. 40 ml. of absolute alcohol are then mixed in and the phases allowed to separate. If a clear solution is not obtained a little ether may be added. The insoluble portion is filtered off and



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Fig. 6 — FILTERING OFF UNDER REDUCED PRESSURE THE PRECIPITATE IN THE DETERMINATION OF SODIUM AND WASHING IT WITH THE REAGENT

may contain highly polymerised compounds, miscellaneous impurities originally present and inorganic salts. These last may be extracted with water. 50 ml. of water and 50 ml. of concentrated hydrochloric acid are then added to the alcoholic solution and the mixture refluxed for at least an hour, bumping being prevented by the addition of a pinch of pumice or a little porous pot. Although true sulphonic acids are not decomposed by this method, they generally are thrown down by the acid. When cool, the mixture is poured into a separating funnel, separated and the clear acid layer tested with barium chloride for the presence of sulphuric acid. The oil is then neutralised carefully, mixed with a fusion mixture, composed of equimolecular proportions of sodium carbonate and potassium carbonate, dried and fused. When cool, the melt is dissolved in water and tested with barium chloride for sulphates.

Acidity.

The acidity of a sulphated oil used in the finishing processes is very important, as if too acid it would hasten the deterioration of the leather, while if very alkaline, a poor colour will be obtained. Both the acid value and pH value should be determined.

Acid Value.

This is determined in a manner similar to that used for the acid value of unsulphated oil.

1 g. of the sample is dissolved in a mixture of 20 ml. of 95 per cent. alcohol and 20 ml. ethyl ether and the solution titrated with tenth normal alcoholic potassium hydroxide, using phenolphthalein as an indicator. A blank determination should be made on the mixed solvents and the titration thus obtained subtracted.

pH Value.

The pH value of a solution of 1 g. of the oil in 250 ml. of water may be determined by using the glass electrode apparatus.

Some Simple Tests of Substances Used in the Finishing Processes.

It is often necessary to be able to test rapidly the purity of the materials used

for finishing leather when a complete chemical analysis is not convenient.

Dried Blood.

The determination of the ash is the usual test applied to this material. The ash should be between 4 and 5 per cent. and should be white. A brick red colour would indicate adulteration with iron compounds.

Dyestuffs.

The following procedure is one whereby a dyestuff may be tested to see whether it is a single substance or a mixture. A small portion of the dye is placed on the end of a spatula or pen-knife blade and blown on to a piece of wet white filter paper, placed about a foot away. The small particles will then adhere to the damp paper, dissolve in the water and show up the colour.

Egg-yolk.

This material is usually analysed for moisture content by drying in an oven at 100° C.; for ash by igniting at a low temperature in a platinum basin; for fat by extraction with light petroleum, and for nitrogen by the Kjeldahl method.

Glucose and Gum-Arabic.

If a little glucose is burnt on a piece of platinum foil, only a small amount of ash should remain.

Gum-arabic should be completely soluble in ammoniacal copper sulphate solution.

Shellac.

Shellac may be contaminated with sand or weighting material. A good sample should be completely soluble in either hot methylated spirits or hot ammonia solution.

Soaps.

The sample should be cut into small pieces and boiled with absolute alcohol. Only soap will dissolve, leaving any "filling" material behind.

Detection of Iron.

Iron is best detected by ashing the material in a platinum crucible at a low heat, cooling and treating with a few drops of strong nitric acid and dissolving in dilute hydrochloric acid. The solution is then treated with a 10 per cent. solution of potassium thiocyanate. A blood-red colour indicates the presence of iron.

SULPHURIC ACID MANUFACTURE

THE LEAD CHAMBER PROCESS

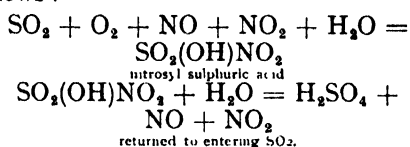
By M. D. CURWEN, B.Sc., A.I.C.

IN a previous article the method of producing sulphuric acid by the contact process (using platinum, iron oxide and vanadium catalysts) was described, it being preceded by a description of the manner in which the gas sulphur dioxide was prepared from pyrites, sulphur, blendes, and so on. As these methods of producing sulphur dioxide are essentially the same as those applied in the lead chamber process, they will not be repeated here.

The chamber process is by far the older of the methods, having been established in a crude way in the early part of the 19th century and, except for important mechanical improvements and the introduction of a new method of applying the catalyst used, has scarcely changed since.

In essence the process consists in the addition of water (in the form of spray or steam) and of oxides of nitrogen (the catalyst) to sulphur dioxide, to form an intermediate compound known as nitrosyl sulphuric acid. This is decomposed to form sulphuric acid and oxides of nitrogen, which latter are removed to enter the system again at the beginning. It is thus an oxidation reaction of sulphur dioxide to sulphur trioxide, the oxides of nitrogen (actually a mixture of nitric oxide NO and nitrogen peroxide NO₂, the latter being formed from nitric oxide) acting as the oxidising agent or oxygen carrier.

Thus the reactions can be formulated as follows :—



Plant Required.

The chief items of plant required for this process consist of the machinery required for producing sulphur dioxide and its purification; secondly, an apparatus for producing oxides of nitrogen and passing them into the sulphur dioxide stream; thirdly, a Glover tower, which acts as a cooler for the above gases before they enter the chambers, and also as an acid-denitrator and acid-concentrator; fourthly, the chambers; and, fifthly and last, the Gay-Lussac tower, which receives the exit gases from the chambers and removes the oxides of nitrogen they contain.

Sulphur Dioxide Burners.

These have already been described and

may be of the rotary horizontal type, such as the Glenville; the circular hearth type with rotating arms, such as the Herreshoff; or the rectangular hearth type, such as the Harris furnace. Pyrites, mineral sulphur (brimstone) and spent oxide

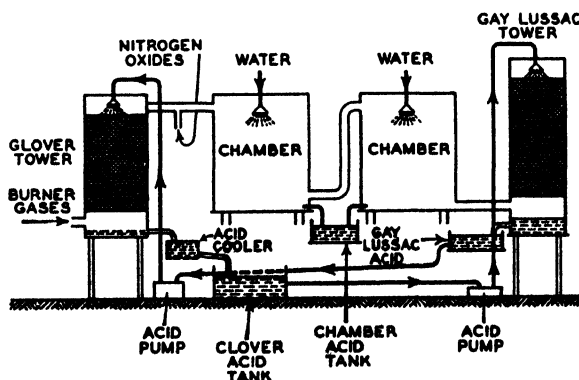
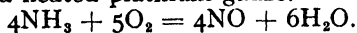


Fig. 1.—DIAGRAMMATIC SKETCH SHOWING FLOW OF GASES AND ACID THROUGH CHAMBER PLANT.

are the common raw materials used in the chamber process. The last named cannot be used for the contact process. The burner gases containing from 5 to 10 per cent. of sulphur dioxide, together with oxygen and nitrogen from the air, pass through dust-collecting chambers and electrical precipitators to purify them.

Oxide of Nitrogen Production.

The furnace gases are then supplied with a proportion of oxides of nitrogen. Formerly this was universally carried out in an iron pot in which nitrate was treated with sulphuric acid, the resultant gases passing into the sulphur dioxide flue. To-day it is more general to oxidise ammonia by passing the latter with air over a heated platinum gauze.



This method is much cheaper than the use of the nitre-pot, which is rapidly being superseded. Here the introduction of the oxides of nitrogen may take place between the Glover tower and the first chamber.

The Glover Tower.

The gases, at a temperature of $300^\circ\text{C}.$, are now led to the base of a tower made of lead and protected by a lining of brick. It is usually some 35 feet high and 15 feet wide. At the point where the gases enter the Glover is an empty space for the circulation of the gases and the collection of acid, but above it and supported on strong arches are layers of packing material, which distribute acid sprayed in from the top. The function of this tower is three-fold. As the gases are still too hot to enter the chambers, the cold descending acid serves to cool them to the requisite temperature ($80^\circ\text{C}.$), and secondly, the acid descending is not only cold but dilute, having been pumped from the chambers and the Gay-Lussac tower, so that the Glover also acts as a concentrator, hot and fairly strong acid (about 78 per cent.) being removed from the bottom. Furthermore, this tower, having received the acid (laden with oxides of nitrogen) from the bottoms of these chambers and the Gay-Lussac tower, thus supplies the gases going to the chambers with a large proportion of oxides of nitrogen. It will be realised that the function of the nitre-pot is to supply

only "make-up" oxides of nitrogen lost in the process.

As will be understood, the acid obtained from the Glover tower is the finished acid (about 78 per cent.), but although much acid of this strength is required in industry, a still more concentrated acid is also needed. For this purpose it is concentrated by means that will be described later.

From the Glover tower the reacting gases pass into the chambers at about $80^\circ\text{C}.$

The Lead Chambers.

These, as the name indicates, are merely large boxes made of sheet lead, adequately supported on a strong framework which may be of wood or steel, and varying greatly in size (very roughly 100 feet long and 30 feet high, if they are box-shaped). They also vary in shape, a modern form being that of a truncated cone which can thus be cooled on the outside by a stream of water. Space is a great consideration, and this type reduces the chamber space enormously.

In the chambers most of the formation of sulphuric acid takes place, although, of course, some sulphuric acid is also made in the Glover and Gay-Lussac towers. Water is sprayed into the chambers and must be carefully regulated, since if the quantity supplied is too small to bring about the total hydrolysis of nitrosyl sulphuric acid, crystals of this substance immediately form on the floors and cause corrosion. The strength of the sulphuric acid formed in the chambers is about 60 per cent., and is removed through acid coolers to storage. Usually this low-strength acid finds a considerable outlet in industry, but since stronger acid is also required, much of it is concentrated to about 78 per cent. in the Glover tower, as already described.

The Gay-Lussac Tower.

Most of the sulphur dioxide has now been converted to sulphuric acid in the chambers, but a small quantity in the form of nitrosyl sulphuric acid leaves the chambers with the exit gases. As it is highly desirable to recover all the acid and the nitrogen oxides (apart from the fact that such gases and vapours must not be allowed to pollute the atmosphere), the

exit gases are passed through the Gay-Lussac tower or, as it is sometimes called, the cold tower, in contradistinction to the Glover, which is a hot tower. Some of the acid obtained from the Glover

with a strength of about 78 per cent. is pumped to the top of the Gay-Lussac, which is also filled with an acid proofing packing, and is sprayed on to this packing to trickle down. It thus removes all the oxides of nitrogen contained in the ascending gases and finally collects at the base of the tower and is removed to a storage tank. This acid, as required, is then, as previously stated, pumped to the top of the Glover tower, where, mixed with the chamber acid, it receives the heat treatment, which removes the nitrogen oxides it contains.

As will be understood, most of the acid made in the system is re-circulated to provide an efficient process.

Purification of Acid.

Much of the acid as produced in the chambers and in the Glover tower finds a wide market without further treatment, but for many other purposes it is not sufficiently pure, since it may contain, depending on the raw material, traces of arsenic acid, antimony oxide, selenium, lead, zinc, mercury, nitric acid, etc. Thus for the "pickling" of brass objects, acid which contains mercury is detrimental and acid containing arsenic is unsuitable for accumulators. Normally, the greatest attention is paid to arsenic and nitric acid. When brimstone is burned, a very pure acid is obtained, but Spanish pyrites results in an acid containing about 0.1 to 0.15 per cent. of arsenic.

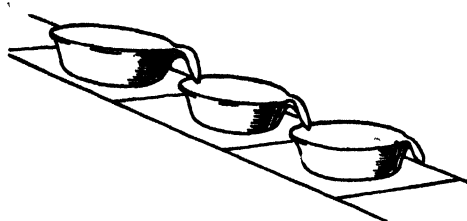


Fig. 2.—THE CASCADE PROCESS.

arsenic acid. Many chemical methods exist for the removal of this metal, such as precipitation by sodium thiosulphate or sulphuretted hydrogen. The latter not only produces arsenic sulphide, which is removed, but also eliminates nitrogen oxides.

Pure sulphuric acid from chamber acid can only be made by fractional distillation, volatile compounds having been previously removed. The distillation may be carried out in glass-lined retorts or in towers using glass rings for fractionation, or in fused quartz (vitreosil) vessels.

Concentration of Acid.

As indicated before, acid is required by industry in a variety of strengths and, furthermore, concentration of acid is not only carried out in acid factories, but also in other chemical and allied industries where acid is used and weakened in the process. As examples of these we may cite the petroleum industry, where acid is used to purify oil, in explosive works, where, together with nitric acid, it is used for the nitration of cotton and glycerine, and in steel and other metal cleaning, where it is used in pickling.

Pan Concentration.

One of the oldest methods is that of pan concentration in which a lead pan suitably protected with an acid-brick lining is heated. Where the quality of acid is not important, the heat is applied from above; other-

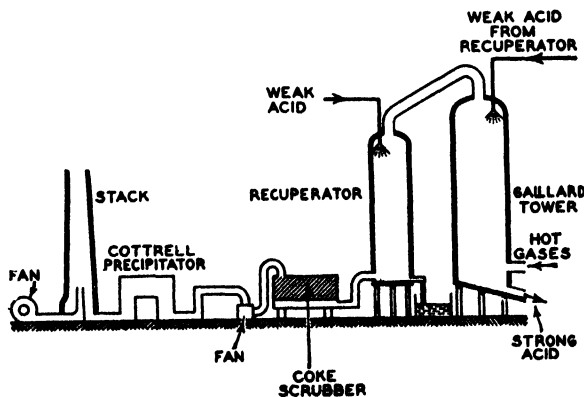


Fig. 3.—THE GAILLARD TOWER METHOD.



Fig. 4.—AMMONIA OXIDATION PLANT SHOWING CONVERTER AND SILICA COOLER.

wise the heat is applied from beneath the pan.

The Cascade Process.

This method is one of the best known and consists in allowing the acid to flow successively from one beaker or dish into another placed immediately below it. The dishes (about 30 in number) are arranged on an inclined structure, the lip of one projecting over the next, the series resting on seats of obsidianite and are heated by flues below.

The Kessler "Saturex."

This method is widely employed and consists in passing the hot gases from a gas-producer over a large surface of the acid. In essence the plant consists of the "Saturex," a shallow trough made of volvic lava which is surmounted by a recuperator consisting of five superimposed trays, fitted with luted bells to allow the upward passage of hot gas and the downward passage of acid, the latter being fed into the top of the recuperator and trickles down to the trough.

The Gaillard Tower.

Many modern apparatuses for concentrating acid have appeared on the market, and of special note are the new towers, built completely of vitreosil—towers fitted with shelves down which the acid trickles, getting more concentrated as it reaches the

bottom. For the present purpose we may conclude, however, with an exposition of the Gaillard tower, which was widely used in this country during the war, especially for the concentration of weak acid obtained from the manufacture of explosives.

Essentially this method consists in spraying acid down a tower in which hot gases from a gas-producer are forced upwards. The accompanying sketch (Fig. 3) (see "The Concentration of Sulphuric Acid," by J. W. Parkes) shows the more complete plant, such as that employed at Queen's Ferry during the war. Weak acid is sprayed down the Gaillard tower, up which hot gases pass from a gas producer. Water is thus removed from the acid and the concentrated liquid collects at the foot of the tower and is removed. The hot gases pass out of the top and into the head of a second tower or recuperator, where the heat is employed to give a partial concentration to weak acid, which also is sprayed in from the top. This partially concentrated acid is pumped to the top of the Gaillard. From the recuperator, the gases issue from the bottom and enter first a scrubber and then a Cottrell precipitator to remove acid mist, and are finally exhausted to the air up a chimney stack.

This type of plant concentrated 70 per cent. acid up to a strength of about 90 per cent.

CONTROL WORK IN SULPHURIC ACID MANUFACTURE

EXAMINATION OF RAW MATERIALS

By W. H. IBBOTSON

IT has been mentioned in a previous article that the sulphur dioxide gas destined to be treated by the contact or the chamber process to produce sulphuric acid is derived not only from native sulphur but also from other materials—spent oxide of gasworks, pyrites and zinc blende. The gases produced from these various materials differ considerably in composition, this having an influence in the manufacturing process and on the quality of acid produced. It is therefore necessary in practice to examine such sources of sulphur as may be used to ascertain their value. Some consideration of the constitution of the materials mentioned above is necessary.

Brimstone or Crude Sulphur.

This material provides the purest gases for the purpose of manufacturing sulphuric acid. As will be seen on page 64 the American variety is exceptionally pure. The Italian sulphur may not reach so high a standard of purity, but the slight impurities are not such as to prejudice its use for production of high-grade acid. Some forms of native sulphur unfortunately carry small quantities of arsenic, selenium or bituminous matter. The latter interferes with satisfactory burning and the two former are elements undesirable in the acid. Italian sulphur, however, is usually free from all such matter, and such impurities as it contains, probably to a total of 2 per cent., are mineral matter such as gypsum, which remains as ash to be discharged from the burner.

Spent Oxide.

This material has some relation to brimstone in the fact that the sulphur is in a free state, whilst in the case of pyrites and

zinc concentrates the sulphur is combined as sulphides. This, however, is the only likeness that spent oxide bears to any other material, being a complex and most inconstant mixture. Before use in the town's gas purification process the hydrated iron oxide or bog-ore is far from being a chemically pure compound of iron, containing as it does a large proportion of woody matter and mineral compounds. After use in contact with the impure gas it has become contaminated in various degrees by many products of the distillation of coal in addition to salts formed by the reaction of these products with the iron compounds originally present. The substance which has appeared as a result of the gas purification to be of importance for the purpose of acid manufacture is the free sulphur derived by the removal of sulphuretted hydrogen from the crude gas. Essentially, the oxide has first become sulphides of iron and the subsequent oxidation or revivification by air exposure has caused decomposition of these sulphides, the iron again being oxidised to oxide and the sulphur being precipitated in the free state. (See Coal Gas Purification.)

The impurities in the spent oxide which have influence on its use for acid manufacture are principally woody matter, ammonia, salts of ammonia and tarry matter.

Tests on Brimstone and Spent Oxide.

The estimation of sulphur is the principal test for evaluating both these materials containing their sulphur in the free state. Advantage is taken of the fact that sulphur is soluble in carbon disulphide and actually an extraction of the sulphur present in each case is made. However, when dealing

with spent oxide the resulting extract is not pure and is treated to separate sulphur and to estimate tarry matter. This will be dealt with in due course. The first part of the sulphur test on both spent oxide and brimstone is the same.

Preparation for Sulphur Test on Brimstone and Spent Oxide.

The thoroughly mixed sample is prepared by being first rapidly ground in small portions so as to pass a 20-mesh sieve. Some oxides are received containing considerable amounts of water, possibly 25/30 per cent. These are of course impossible to sieve and grinding must be carried out in a mortar to the best advantage. Brimstone is usually almost dry. A representative portion of the whole remixed sample is dried for two hours or more in a hot-water oven at 100° C. The dried sample is then reground in a dry mortar until of a floury fineness and placed in a porcelain dish in a desiccator until thoroughly cooled.

Method of Estimating Sulphur.

In the actual process of extraction a Soxhlet extractor is used, the brimstone or spent oxide being contained in a thimble made of specially prepared filter paper. A convenient size is 22 × 80 mm. The thimbles are obtainable in a nominally fat-free condition, but each should be treated by extraction with carbon disulphide to remove any soluble material. The carbon disulphide used must also be redistilled before use. In conjunction with the extractor a glass extraction flask is used to receive the sulphur in solution from the extractor.

Weighing out the Material Under Test

The dish containing the dried reagent brimstone or spent oxide is taken from the desiccator and the contents rapidly mixed with a clean spatula, the edges being dusted inwards with a camel hair brush and the underside being dusted. The dish and contents are rapidly weighed (to the nearest milligram in the case of spent oxide, and to one-tenth of a milligram in the case of brimstone) to avoid absorption of moisture from the atmosphere.

Transferring to Extractor Thimble

The weight having been noted, the sample is carefully transferred by the

prepared extraction thimble. Practice enables the worker to gauge the amount transferred, which may be anything from one to two grams. After transfer, any material adhering to the spatula is brushed back to the dish, which is then reweighed and the weight again noted. The difference in weight indicates the amount of dry material taken.

Setting up the Apparatus.

Similarly, the clean, dry extraction flask is weighed and is charged with sufficient redistilled carbon disulphide to fill the Soxhlet extractor and provide for an excess of about 20 c.c. A convenient size extractor being 60 c.c. capacity, thus about 80 c.c. are required. Any possibility of passage of solid material from the extractor by splashing or porosity of the thimble must be guarded against, and it is, therefore, usual to place in the bottom of the extractor a wad of cotton wool which has been subjected to previous extraction with carbon disulphide. This wad acts as a further filter, and on this in turn is placed a small coil made from glass rod on which the thimble rests. The whole apparatus is then set up on the water-bath.

The
cr

of the pure disulphide may be done direct to the stock bottle. Replacing on the bath, distillation is continued until the bulk remaining in the flask is only two or three c.c. The flask is then removed and the extract is distributed around the inner surface by gently turning, keeping inclined whilst so doing. The result of this is that the remaining carbon disulphide evaporates from the warm surface and the sulphur appears as a thin crystalline film inside the flask.

Finishing the Test.

The flask is next wiped clean and dry on the outside and blown out, then transferred to the hot water oven, there to be dried at 100° C. for about half an hour. It is advantageous to blow out the flask at intervals during this period to remove heavy vapour of disulphide. After drying the flask is cooled in a desiccator for a further half-hour and then reweighed. The increase in weight is due to the extracted sulphur (and other soluble matter in the case of spent oxide) from the known weight of dry material. To complete the estimation of sulphur in the material as received it is necessary to take the moisture into consideration.

Calculation of Sulphur Percentage.

The moisture figure obtained in the manner indicated above is employed in calculating the sulphur in the original material thus:—

	Spent oxide. gms.	Brimstone. gms
First weight of dish and dry material	38 255	37 3592
Second weight of dish and dry material	37 055	36 2342
Dry material extracted	1 200	1 1250
Weight of flask and dried extract	45 517	47 3550
Weight of flask alone ..	44 706	46 2414
Weight of extract ..	0.811	1 1136

Sulphur (including tarry matter)	Sulphur.
$= \frac{0.811 \times (100.0 - 22.3)}{1.200}$	$\frac{1.1136 \times 99.8}{1.1250}$
$= \frac{0.811 \times 77.7}{1.200}$	
= 52.512 per cent.	= 98.789 per cent.

Tarry Matter.

In the case of brimstone, the extract weighed and calculated as above may be taken as pure sulphur. With spent oxide, however, tarry matter may be present in some quantity and its presence can be observed in the colouring of the extract. In some oxides it is negligible, but if the extract is dark in colour, the sulphur content determined as above is not conclusive, and separation of sulphur is achieved by the following method, which is inherently satisfactory for works purposes.

Further Treatment of the Spent Oxide Extract.

The dried, cooled and weighed extract is added about 20 c.c. of strong sulphuric acid (94 per cent. H_2SO_4) and the mixture is heated for a half-hour in the water bath at 100° C., being gently shaken at intervals so that the hot acid comes in contact with the whole film of extract. During this treatment the flask is removed to cool and then to the mixture is added about 150 c.c. of cold distilled water, agitation being made cautiously and in small quantities per a washbottle jet, the flask throughout the operation being cooled, which may be facilitated by externally applied cold water,

the whole contents of the flask are filtered through a close filter paper, which after filtration must be washed until free from acid as indicated by a blue litmus paper. The washed flask, funnel and filter paper are then transferred to the oven, and when drying is completed the paper is removed from the funnel and is carefully inserted into the extraction thimble, replaced in the Soxhlet extractor to which is attached the dried flask, and the extraction as conducted on the original oxide is repeated. The purified contents of the flask will this time represent pure sulphur, and the tarry matter will be deduced from the difference in extracts.

Thus :—

Weight of flask and second extract	45.477
Original weight of flask alone	44.706
	0.771

$$\text{Pure sulphur} = \frac{0.771 \times 77.7}{1.200} = 49.922$$

Therefore, the amended result will appear :—

	Per cent.
Drying loss reckoned as H_2O =	22.3
Pure S =	49.922
Tarry matter =	2.59

Testing Sulphur for Impurities.

The impurities to be looked for as important to the acid manufacturer are arsenic and selenium, sulphur being used for the production of the highest grades of acid, and it is desirable that it should be free from these impurities. In the case of arsenic, use is made of the fact that it is present in combination with the sulphur, and the sulphide is soluble in dilute ammonia solution.

Estimation of Arsenic.

To estimate the arsenic in the ground sulphur, a known weight of the latter, say 5 gm., is digested with dilute ammonia and after digestion the whole is filtered and the paper thoroughly washed, washings being added to the filtrate. The liquor is next evaporated to dryness, a little nitric acid added and again evaporated. An addition of about 10 c.c. of pure dilute sulphuric acid is then made and, after heating, this acid solution is treated as is

sulphuric acid in the modified Gutzeit arsenic test, dealt with on page 442.

Selenium.

This is detected if present by fusing a portion of the ground sample with potassium nitrate and, after cooling, dissolving the mass in hydrochloric acid. The filtered acid solution is treated with sulphur dioxide, which precipitates any selenium.

Ammonia in Spent Oxide.

Ammonia present in the material burned is an important factor in "nitre" consumption in the chamber process, so examination is desirable to ascertain the amount present, any quantity over 1 per cent. being regarded as undesirable whether present as free ammonia or as salts.

The test is carried out by distilling 5 gm. of the oxide with about 100 c.c. of distilled water and 50 c.c. of caustic potash or caustic soda solution (specific gravity 1.25), with the addition of a small piece of paraffin wax. The ammonia and steam evolved pass through a distillation head into a receiving flask, externally cooled by immersion in cold water, in which has been placed 10 c.c. of normal sulphuric or hydrochloric acid and 50 c.c. of distilled water. Distillation proceeds until all ammonia has been expelled, about 15 minutes sufficing, and the contents of the receiving flask, after cooling, are titrated to neutrality with normal alkali, methyl orange being used as indicator.

Calculation of the Ammonia.

The difference between the volume of normal acid in the receiving flask and the volume of normal alkali used to neutralise after distillation is thus the volume of normal acid neutralised by the ammonia evolved from 5 gm. of oxide. As 1 c.c. normal acid is equal to 0.017 gm. NH_3 , the ammonia present is calculated as in the example below :—

Normal sulphuric acid in flask	10	c.c.
Normal alkali used	7.00	c.c.
∴ Normal acid neutralised by evolved ammonia	3.00	c.c.
$3 \times 0.017 = 0.051$ gm. NH_3		
Weight of oxide taken—5 gm.		

Then per cent. NH_3 =

$$\frac{0.051 \times 100}{5} = 1.02 \text{ per cent.}$$

Recovered Sulphur.

In passing, it might be noted that some very impure types of sulphur, recovered from chemical processes, are sometimes encountered, and these, if used, are usually burned with other materials, such as spent oxide, which may be enriched by such addition, but impurities may be expected and should be looked for. The notable impurities, often to a marked degree, are usually ammonia and arsenic. These may be detected and estimated by the means outlined above.

Pyrites and Zinc Blende or Concentrates.

In these materials the sulphur is not present in the free state as in the materials already dealt with, but is in combination as sulphides, principally of iron or zinc as the case may be. The method used to estimate sulphur must, therefore, be different to that for spent oxide. In this instance the sulphides are attacked by strong oxidising mineral acids to obtain the sulphur in solution as sulphate which can be precipitated as an insoluble salt.

Pyrites—Preparation for Testing.

If dry or almost dry the sample must be first finely ground and, after mixing, be kept in a well-corked bottle from which portions for analysis are weighed as required. Should it be exceptionally wet, as sometimes happens in the case of common "fines," it will be advantageous to dry an average portion at 100° C., grinding to the requisite fineness after drying and thereafter analysing on the dry basis, a separate portion being tested for moisture by drying at 100° C. to obtain a correction figure to convert "dry" analysis to the wet basis.

Estimation of Sulphur in Pyrites.

It will be found that 0.5 gm. is a convenient weight to employ. This weight of pyrites is placed in a beaker and to it is added about 10 c.c. of a mixture of nitric and hydrochloric acids in the proportion of three parts nitric (1.4 specific gravity) and one part hydrochloric. The beaker is then heated, gently at first, until the pyrites is dissolved, whilst care is taken to avoid any loss which might be occasioned by violent action, by keeping a cover glass in position on the beaker.

Drying and Redissolving.

On completion of solution the contents

of the beaker are evaporated to dryness on a waterbath or hotplate after the addition of about 0.5 gm. of pure sodium chloride to fix the sulphur. After drying and cooling sufficiently, 5 c.c. more of hydrochloric acid is added and again the solution is evaporated to dryness. The next operation is the treatment of the dried residue with 100 c.c. of hot distilled water together with 1 to 2 c.c. hydrochloric acid and after digesting, the contents of the beaker are filtered, the paper being thoroughly washed and the washings added to the filtered solution.

The Insoluble Residue.

The residue remaining on the filter paper contains not only silica but also insoluble sulphates of metals and alkaline earths. The sulphur thus combined, however, is not available for use in the production of sulphur dioxide and can be disregarded. The filter paper, after thoroughly washing, is dried and ignited to give a figure for insoluble matter.

Further Treatment of the Filtrate.

The combined solution and washings are saturated with ammonia, sufficient dilute ammonia solution being added to precipitate the whole of the iron in solution with a slight excess, evident by the smell. After agitation, the alkaline mixture is heated gently until all excess ammonia is driven off (but boiling is avoided), is then filtered whilst hot, and the filter paper and precipitate thoroughly washed until the washings cease to give a precipitate with barium chloride solution.

Precipitation of Barium Sulphate.

Having thus obtained a solution containing the available sulphur, preparation is made to precipitate it as barium sulphate by acidifying the combined filtrate and washings with a slight excess of hydrochloric acid. Should the bulk be large, this is reduced by evaporation to a volume of 200-250 c.c. prior to acidification. Acid having been added, the solution is brought to boiling point and about 20 c.c. of a 10 per cent. solution of barium chloride, also boiling, is added. Care is taken to avoid loss by ceasing to heat the beaker at the moment of adding the barium chloride. Addition being completed, the mixture is boiled gently and the precipitate is allowed to settle.

Completing the Test.

The precipitate is collected on a close filter paper of known ash weight, by filtration, and washing with distilled water is carried on by decantation and wash-bottle until the washings cease to be acid or to contain barium chloride as indicated by sulphuric acid. The funnel and paper are then dried at 100° C. and the paper and precipitate ignited, by the method of folding, wrapping in a coil of platinum wire and burning over a crucible. The crucible is then placed in the muffle furnace until the precipitate remains as a fine powder.

Calculation of Results.

After removal from the furnace and complete cooling in the desiccator, the crucible is weighed to the nearest 0.0001 gm., and is then emptied, brushed clean and reweighed. The difference is due to barium sulphate, plus the filter ash, which is deducted. Barium sulphate contains 13.743 per cent. of sulphur; therefore, if the weight of precipitate be multiplied by 0.13743, the weight of available sulphur will be obtained. Having taken 0.5 gm. of pyrites, multiplication of this weight of sulphur by 100 and division of this figure by 0.5 will give the percentage of sulphur in the pyrites.

Estimation of Sulphur in Zinc Blende.

This material is tested in a manner very similar to that used for pyrites. Preparation for analysis is the same, but the 0.5 gm. of blende is first decomposed by pure strong nitric acid until the first violent action is completed, when solution is completed by the addition of hydrochloric acid drop by drop, gentle heat being applied. Any iron present is removed by ammonia precipitation as in the pyrites test, and the sulphate is precipitated by barium chloride.

Occurrence of Arsenic in Pyrites and Blende.

Unfortunately for the acid manufacturer, arsenic often appears in this class of material, although some ores commercially free from the element are obtainable. Consequently the estimation of arsenic is important.

Estimation of Arsenic.

The method applicable to works purposes is that of Reich modified by M'Kay.

Again 0.5 gm. of pyrites or blende is employed, this being decomposed by pure nitric acid in a large porcelain crucible. The crucible is heated gently until all free acid is driven off, but not to complete dryness, then 4 gm. of sodium carbonate is added to the moist contents. Heating, preferably on a sandbath, is continued until the mass is quite dry, when 4 gm. of potassium nitrate is added. The crucible is then more strongly heated until the contents are fused and kept in a state of fusion for about 10 minutes.

After being allowed to cool, the fused mass is washed from the crucible into a beaker with hot water and the resultant solution is filtered, the paper being thoroughly washed and the washings added to the filtrate. The solution is then acidified with a little nitric acid and heated gently until all CO₂ has been driven off.

Precipitating.

To the solution, 5 c.c. decinormal silver nitrate is added and this addition is followed by exact neutralisation with dilute ammonia. The precipitate which has appeared, Ag₃AsO₄, is then dissolved by pouring on the paper hot dilute nitric acid (one part acid to one part water) in small portions to a total of about 10 c.c. The arsenic present is then estimated indirectly by estimation of the silver in the nitric acid solution, titrating with decinormal potassium thiocyanate and using an indicator in the form of 2 c.c. of a solution of iron alum from which the brown colour has been discharged by addition of nitric acid.

The Titration.

The thiocyanate, which must be previously standardised against decinormal silver nitrate, is added to the nitric acid solution of the precipitate until a permanent red coloration is observed.

The thiocyanate solution, if of correct strength, should be equivalent to 0.01079 gm. silver, and thus will be equivalent to 0.002499 gm. arsenic per c.c.

Example:—If *a* c.c. be volume of thiocyanate used, then

$$\frac{0.002499 \times a \times 100}{0.5} = \text{per cent. As.}$$

Materials Used for Supply of "Nitric."

As will have been gathered from earlier sections describing the chamber process,

nitrogen oxides play a part and must be constantly supplied to make up losses. These supplies are derived from nitric acid, nitrate of soda "potted" with sulphuric acid, or nitrogen oxides produced by the catalytic oxidation of ammonia. It is therefore necessary to test these materials, whichever may be used.

Nitric Acid.

The acid used for this purpose is usually what is known as "80 Twaddell," that is, a density of 80° on the Twaddell hydrometer at 60° F., equivalent in pure nitric acid to 65.3 per cent. HNO_3 . In commercial nitric acid of this description the comparison of gravity to percentage HNO_3 is not always exactly true, but as it is usually bought on a gravity basis, the checking by hydrometer is usually sufficient. Where other strengths than that mentioned above are used, the hydrometer reading can be readily compared to the tables of nitric acid strengths and gravities available in many works of reference.

If it be thought necessary to test the acid by chemical means, this is done by making up a solution from a weighed quantity and treating a portion of this in the nitrometer in a similar manner to that which will be described later in dealing with the testing of nitrous sulphuric acid.

Nitrate of Soda.

This material is not universally tested on the same basis. The nitrate trade estimates moisture, sodium chloride and sulphate, and insoluble matter, assuming the remainder to be nitrate of soda. It is, however, preferred by some users to estimate its value in nitrogen content.

Testing the Nitrate.

The sample should be very carefully taken in such a manner as to be truly representative of the consignment. Moisture is estimated in a similar manner to that adopted for sulphur, etc., except that drying is carried out in a hot-air oven kept at 130° C. for about four hours, and the final cooled weight is confirmed by further heating until no further loss is observed.

Insoluble Matter.

This is estimated by first dissolving 10 gm. in about 200 c.c. of distilled water in a 250 c.c. graduated flask, making up to

the mark on completion of solution. The solution is filtered and is then reserved for use in later estimations, the insoluble matter being thoroughly washed on the paper. The filter is then dried and ignited in a crucible. The weight of ash remaining, less the weight of filter ash, represents the insoluble matter in 10 gm. of nitrate. Thus, multiplication by 10 gives percentage.

Estimation of Sulphates.

Sulphates are estimated by taking 100 c.c. of the solution reserved from the insoluble matter filtration. Obviously this volume contains $\frac{1}{10}$ of the original 10 gm. taken, that is, 4 gm. The solution is slightly acidified with hydrochloric acid and the sulphates are precipitated with barium chloride and weighed as in the sulphur estimation in pyrites. The conversion of the barium sulphate obtained to sodium sulphate follows thus— $\text{BaSO}_4 \times 0.6086$, and the percentage obtained by a further multiplication by 25.

Estimation of Chlorides.

A further 100 c.c. of reserved solution as in the above is taken for this estimation. To this is added sufficient neutral potassium chromate solution to give a yellow colour, and titration with decinormal silver nitrate is proceeded with until the precipitate formed is faintly but distinctly pink. A slight deduction, say, of two drops of 0.1 c.c. of the silver nitrate used is made, to allow for the colour production, 1 c.c. of the decinormal solution being equal to 0.005846 gm. sodium chloride, then

$$\frac{\text{the c.c. used} \times 0.005846}{4} \times 100$$

= per cent. sod. chloride.

Estimation of Nitrate.

Where this estimation is thought desirable it may conveniently be carried out in the nitrometer, the further use of which in the sulphuric acid process will be dealt with later.

The Nitrometer.

In its simplest form this consists of two glass tubes connected at the bottoms by heavy-walled rubber tubing. One tube is plain and open at the top, serving as a levelling tube—the other is graduated, usually to 50 c.c., is contracted at the top

and is surmounted by a cup, communication between cup and tube being made or interrupted by a glass stopcock. Mercury is placed in the apparatus in such quantity as to fill the graduated tube and communicating rubber tubing whilst filling the lower part of the levelling tube to a height of two or three inches from the bottom.

Briefly, the method of using the apparatus consists of the introduction of the material to be tested together with strong sulphuric acid into contact with the mercury in the closed graduated tube, where, when agitated, it is decomposed with evolution of nitric oxide.

Testing Nitrate in the Nitrometer.

As only a very small amount of nitrate must serve for this type of analysis, it is advisable to dry about 20 gm. of the carefully averaged sample in the same way as is done with the moisture test portion. This is then ground and carefully mixed, and is used to estimate the nitrate, bearing in mind, of course, that a moisture correction will be necessary.

About 0.1 gm. of the prepared sample is accurately weighed out, placed in the cup of the nitrometer and 0.5 c.c. of water is added. After the nitrate has been completely or almost dissolved the solution is allowed to enter the nitrometer through the tap, which is then again closed. A further 1 c.c. of water is placed in the cup and this also is passed in. This is followed by 5 c.c. of pure strong sulphuric acid and finally a further 10 c.c. to complete the transfer of the whole of the nitrate into contact with the mercury.

The nitrometer is then shaken until completion of the reaction, when it is clamped up with the mercury at equal levels in both columns to be cooled for a half-hour. When the contents of the nitrometer have cooled to atmospheric temperature, the volume of NO evolved is measured by placing in the cup a few c.c. of sulphuric acid (of about 1.8 sp. gr.), unclamping the reaction arm, holding this close to the other arm in such a position that the level of the mercury is slightly lower than in the open arm, then opening the tap and rapidly adjusting the level of the reaction arm so that no acid flows in or gas escapes. The volume is read off and corrected for temperature and barometric pressure to 0° C. and 760 mm.

Each c.c. of NO is equivalent to 0.0037963 gm. of nitrate of soda. Thus, if the corrected volume of NO be a c.c., and b the weight of nitrate taken, the percentage NaNO_3 in the dried prepared sample is
$$\frac{0.0037963a \times 100}{b}$$

or, corrected for moisture,

$$\frac{0.0037963a \times (100 - \text{per cent. moisture})}{b}$$

Ammonia for Oxidation to Nitrogen Oxides.

In many works ammonia solution is used as the source of nitrogen oxides. It is necessarily of a high degree of purity, this being essential for efficient oxidation and, therefore, the gravity as measured by a suitable hydrometer is a fair indication of the percentage of ammonia. Where accurate estimation is desired, however, the following method gives the most exact result. The nature of ammonia solutions is such as to make accurate testing difficult, ammonia volatilising at the slightest exposure. Samples should be kept in a tightly stoppered bottle.

Apparatus Used.

A stoppered 100 c.c. graduated flask with a short neck is the vessel used for the main part of the test, but in addition a 10 c.c. pipette which has been cut off half-way down the upper portion is required. At the point of severance the pipette has been drawn out and brought to a fine point with a fine orifice. Thus a pipette has been prepared which can be reversed, using the fine orifice for admission and discharge of the contents and the original point for delicate finger control.

The Test.

About 25 c.c. of normal sulphuric acid with a drop of methyl orange is put into the graduated flask and, after replacing the stopper, the flask is weighed. The sample of ammonia is unstoppered and the reversed pipette inserted into the liquor so as to fill without suction, but by immersion only. It is then withdrawn and the contents, retained on withdrawal, of course, by the finger, allowed to run to waste. The outside is then wiped dry and again a portion is taken from below the surface. A drop or two is allowed to escape, the outside of the pipette is wiped dry, one more drop allowed to fall, and then the pipette is

inserted into the neck of the acid flask and the ammonia solution is allowed to run directly into the acid (not down the inner surface of the neck) whilst gently shaking until a point approaching neutrality is reached. A little practice teaches the worker how rapidly the ammonia solution may be added, and the form of pipette used gives complete control of the last cautious additions.

After addition is completed, the flask is restoppered and rapidly weighed once more. Speed is important to avoid errors possible by reason of the heat generated by the reaction.

Completing the Test.

The increase in weight clearly indicates the weight of ammonia solution added. The test is completed by titrating the

contents of the flask with normal alkali.

The volume of alkali required to neutralise the contents, deducted from the volume of normal acid originally charged into the flask, gives the acid neutralised by the ammonia solution. As each c.c. of normal acid is equal to 0.017 gm. NH_3 , then

$$\frac{\text{the weight of ammonia found} \times 100}{\text{weight of ammonia solution}} = \text{per cent. } \text{NH}_3$$

Example :—

25 c.c. N. sulphuric acid taken.	Gm.
Weight of flask, acid and ammonia solution	56.655
Weight of flask and acid	54.650
Weight of ammonia solution	2.005
N. alkali required to complete neutralisation,	
0.35 c.c.	
N. acid neutralised by $\text{NH}_3 = 25.00 - 0.35$ c.c.	
$= 24.65$ c.c.	
$\frac{24.65 \times 0.017 \times 100}{2.005} = 20.90$ per cent NH_3 .	

TURKEY RED OIL

THIS oil (a sulphonated castor oil) is of such widespread use in several industries that a few notes regarding its manufacture may be of use, for it is so simply manufactured that with care it can be made by the small user.

It is very widely used for the production of emulsions of oils and water, including that made for distempers, for the splitting of fats, in soap and candle making, and by textile manufacturers in the treatment of fibres.

Apparatus Necessary.

The plant required is very simple, and if other facilities are not available, a good water-tight barrel fitted near the bottom with a tap is all that is necessary.

Better practice is to use a lead-lined barrel or tank, in which is suspended an

agitator with blades and shaft of wood. Metal tanks must be lined with lead, since sulphuric acid is employed in the manufacture.

Directions for Small Batch.

About 40 lb. of castor oil are poured into the barrel cold, and 9 lb. of sulphuric acid (brown oil of vitriol) is slowly added. The temperature must not be allowed to rise unduly, and should never be more than 30° C. Stand for 24 hours. Then add an equal volume of a saturated solution of salt (brine) to remove the excess acid. Stir vigorously, allow to settle, and draw off the bottom layer of acidulated brine. If the sodium or ammonia salt is required, add a 20 per cent. solution of caustic soda or ammonia until the mixture goes bright.

CHEMISTRY IN THE GAS INDUSTRY

PART VII.—ANALYSIS OF BY-PRODUCTS

By F. E. MILLS, B.Sc., A.M.I.Chem.E.

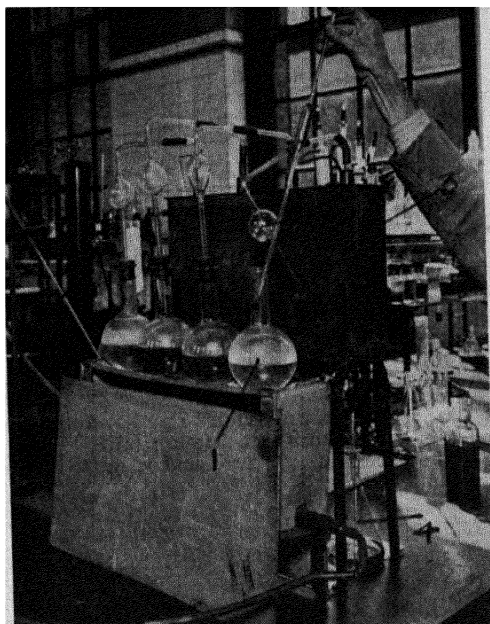


Fig. 1.—DETERMINATION OF AMMONIA IN AMMONIACAL LIQUOR (1).
1, Flask. 2, Splash head. 3, Condenser.
4, Receiver.



Fig. 2.—DETERMINATION OF AMMONIA IN AMMONIACAL LIQUOR (2).
Inserting the splash head prior to distillation for 45 minutes.

AMMONIACAL LIQUOR.

AMMONIACAL liquor is usually pumped direct to the products works if the latter is situated near to the gas works, or it is delivered by means of tank waggons or barges.

Where liquor is despatched by pipe line, a drip sample is taken from the pipe line through a closed sight box into a closed tank, the air vent of which communicates with the air space in the liquor storage tank. When pumping of liquor through the main has stopped, a sample is taken from the tank by means of a dip tube.

Samples from tank waggons or barges are also taken by means of the dip tube,

which consists of a tube of uniform bore fitted with a closure device at its lower end. It is of such a design that a sample can be taken throughout the depth of the vessel to within one inch of the bottom.

When using the dip tube, care should be taken that it is cleaned internally and externally before use, and that the tube is cleaned externally before opening the closure device. Each sample taken with the dip tube is placed in a stoppered bottle and transferred to the laboratory with as little exposure to the air as possible.

Determination of Ammonia.

The apparatus used for the determination of ammonia in ammoniacal liquor is

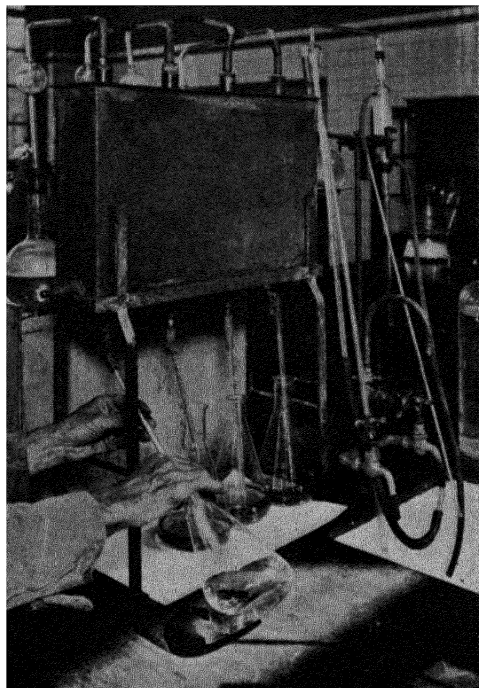


Fig 3 DETERMINATION OF AMMONIA IN AMMONIACAL LIQUOR (3)

The condenser is washed down with distilled water into the receiver.

shown in Fig. 1, and consists of a flask 1, fitted with a stopper and splash head 2, which is connected to a condenser 3. The end of the latter dips beneath the surface of liquid in a conical flask 4 acting as a receiver. An excess of normal sulphuric acid is placed in the receiver, together with enough distilled water to seal the dip pipe from the condenser.

20 ml. of the sample under examination is placed in the flask, previously half filled with water (see Fig. 1), caustic soda solution in slight excess is quickly added to the flask, the splash head is inserted (see Fig. 2), and distillation is continued for 45 minutes.

At the end of the distillation, the condenser is washed down with distilled water into the receiver (see Fig. 3) and the excess of sulphuric acid is titrated with normal alkali solution (see Fig. 4), using a minute quantity of methyl orange, and titrating the solution to exactly the same end point as was used during the standardisation of the solutions.

The strength of ammoniacal liquor is generally expressed by means of the

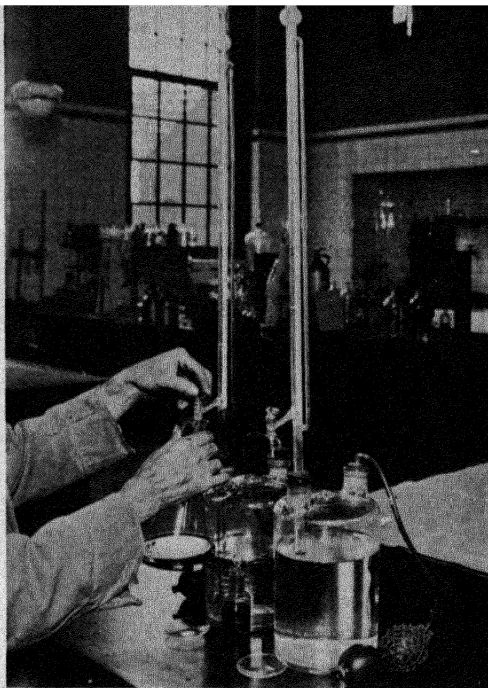


Fig 4 —DETERMINATION OF AMMONIA IN AMMONIACAL LIQUOR (4).

The excess of sulphuric acid is next titrated with normal alkali solution.

rather unusual term "ounce strength." A liquor is of one ounce strength if a gallon of the liquor requires one ounce of pure sulphuric acid to neutralise the ammonia contained in it.

The amount of normal acid neutralised by the ammonia from 20 ml., multiplied by 0.393 gives the ounce strength of the liquor.

SPENT OXIDE.

The sampling of spent oxide follows closely that used for coal, which has been already described in a previous article. When deliveries are being made, daily samples are drawn from each cart or waggon, and collected in an air-tight receptacle. The samples should not be allowed to lie about exposed to the risk of drying, but should be mixed, ground and bottled each day. When the delivery of the parcel is completed, all the daily samples are at once mixed and broken down, using the coning and quartering method.

The well mixed oxide is poured several times on to a given centre so as to ensure the even distribution of both lumps and

finer in the form of a cone. The cone is then flattened and quartered. Two opposite quarters are discarded and the remainder again mixed, coned and quartered, until the quantity is reduced to a convenient amount. This is crushed until it passes through a $\frac{1}{4}$ -in. mesh sieve, when it is at once bottled.

During the above operation, care must be taken to avoid alteration of the moisture content of the sample, which should be at least $\frac{1}{2}$ lb., and is then packed in air-tight bottles and tins only.

Before carrying out the analysis, the whole of this sample is further intimately mixed, broken down and reduced in bulk to about 100 gm., which is then ground so that the whole quantity passes through a 20 mesh sieve.

Moisture.

5 gm. of the sample is dried for three hours at 100° C. in a water oven, cooled in a desiccator and re-weighed. The loss of weight represents the moisture and is expressed as a percentage.

Sulphur and Tar.

The dried residue from the moisture determination is then placed in a Soxhlet extraction thimble (see Fig. 5), which is then extracted for two hours in a Soxhlet's apparatus with freshly distilled, dry carbon bisulphide. The carbon bisulphide is then distilled off, the flask is cautiously blown out with air and dried for two hours at 100° C. in the water oven.

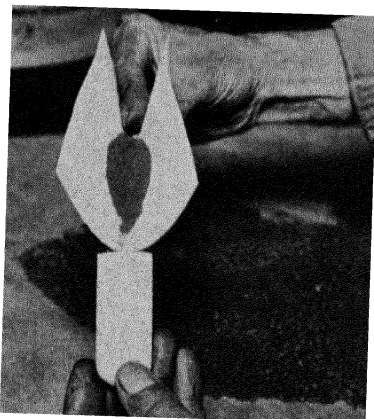


Fig. 5.—DETERMINATION OF SULPHUR IN SPENT OXIDE (1).

The dried sample is placed in a Soxhlet thimble.

Pure Sulphur.

15 ml. of concentrated sulphuric acid is then poured on to the sulphur and tar in the flask, and the whole is heated for two hours at 100° C. in a water oven. After cooling, the contents of the flask are diluted with water, filtered, washed free from acid and dried. The dried filter and its contents are then again placed in the Soxhlet's apparatus and extracted with carbon bisulphide. The bisulphide is distilled off and the residue fused exactly as described above. The

weight of residue now represents the sulphur free from tarry matter, and is multiplied by 20 to give the percentage of pure sulphur.

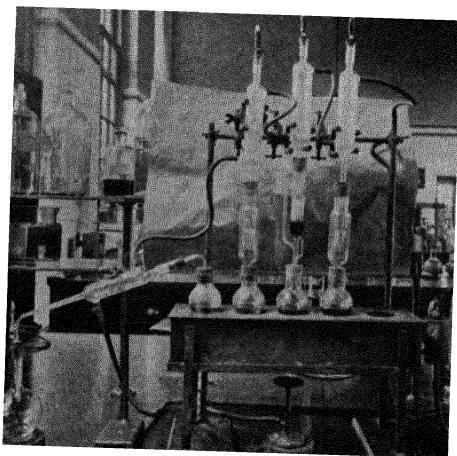


Fig. 6.—DETERMINATION OF SULPHUR IN SPENT OXIDE (2).

Showing a battery of Soxhlet extractors and the apparatus for distilling off the carbon bisulphide.

Fig. 6 shows a battery of three extraction apparatus, together with the apparatus for distilling off the carbon bisulphide.

The flask is then placed on a hot sand bath until the sulphur has just fused, care being taken that no loss by overheating and volatilisation takes place. After the flask has been cooled completely, it is again carefully blown out with dry air and re-weighed. The increase in weight, multiplied by 20, gives the percentage of sulphur plus extracted tarry matter.

CRUDE BENZOLE.

Crude benzole is extracted from gas either by adsorption with active carbon or by solution in a solvent such as gas oil or creosote oil, followed by recovery of the spirit by steam distillation.

For the purpose

of the commercial evaluation of the benzole, the sample is fractionated in the apparatus shown in Fig. 7. This consists of a bolt-head flask 1 of 200 ml capacity, attached to an 8-pear Young column 2, the side tube of which is connected to a condenser 3. A bunsen burner 4 supplies the heat to the flask, a thermometer 5 registers the temperature of the vapour leaving the column, while a 100 ml cylinder 6 receives the condensed liquid. A draught screen 7, of sufficient height to reach the side tube of the column, is placed round the apparatus during the distillation.

100 ml. of the sample is measured into the 100 ml. receiver and its temperature is noted. It is then transferred as completely as possible to the flask. 20 ml. of creosote, which has previously been fractionated through the apparatus to 190°C ., is then measured in the same receiver without rinsing or drying, and is also transferred to the flask, which is then connected to the column and the thermometer inserted. The side tube of the column is connected to the condenser, and the graduated receiver, in which the sample and the creosote were measured, is employed after cleaning and drying, to receive the distillate. The receiver is so placed that the condensate flows

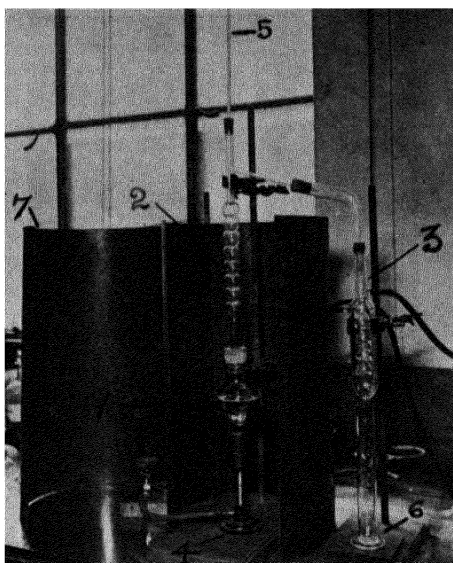


Fig. 7.—EXAMINATION OF CRUDE BENZOLE
1, Bolt-head flask 2, Young column. 3, Condenser. 4, Bunsen burner. 5, Thermometer. 6, Receiver. 7, Draught screen

distillate is brought to the same temperature as that of the original sample, and measured.

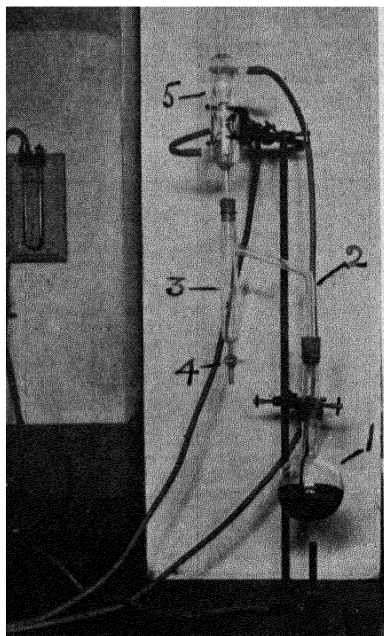


Fig. 8 —DETERMINATION OF WATER IN TAR.
1, Round-bottom flask. 2, Side-tube. 3, Collecting tube. 4, Capillary stop-cock. 5, Condenser.

down its side. The flame is so regulated that the distillation proceeds at the rate of 5 ml. per minute.

The percentage distillate in the receiver is noted immediately the top of the mercury column passes the 100°C . point on the thermometer scale (termed the "running point"), without interrupting the distillation. The fractionation is continued until the top of the mercury passes the 160°C . point (termed the "stop point"), and the apparatus is allowed to drain for two minutes. The

The thermometer readings taken during the test are corrected for the effect of barometric pressure, by allowing 0.5°C . for each 10 mm. pressure difference from 760 mm. This correction is subtracted from the thermometer reading when the pressure reading is above 760 mm., and added to the thermometer reading when the pressure is below 760 mm.

If a visible quantity of water accumulates during the distillation, a separate determination of the water is made and allowed for. The fractional distillation is then carried out on a fresh portion of the sample which has been dried over recently ignited sodium sulphate.

The creosote used is

prepared by fractionating a washed creosote through the specified column to 190° C., rejecting the distillate and using the fluid portion after cooling at a temperature not higher than 15.5° C. for at least two hours.

Bumping during the distillation is minimised by introducing into the flask, before starting the distillation, a small fragment of porous material.

TAR.

Determination of Water.

The sample of tar should not occupy more than two thirds of the volume of the container from which the tar is measured. Immediately prior to the determination of water, the tar in the container is violently agitated for several minutes to distribute any water which may have settled out.

100 ml. is then measured without delay into a 500-ml. round-bottomed flask 1 (see Fig. 8), the measure is washed out into the flask with 100 ml. of crude benzole, and the flask is attached to the side tube 2. This tube delivers into a tube 3, to the bottom of which a capillary stopcock 4 is fused, and to the top of which a reflux condenser 5 is attached. The tube 3 is filled with dry crude benzole or with the distillate from a previous determination. Distillation is commenced by heating with a small flame, and is continued until the water collecting in the lower part of tube 3 becomes constant in volume, at which point the condensing benzole is crystal clear.

The water is then drawn off by the tap 4 into a narrow, finely divided cylinder, and the number of ml. is recorded as the percentage of water by volume.

Free Carbon.

From 1½ to 3½ gm. of the tar is weighed

out of a weighing bottle into a small beaker, mixed with about 25 ml. of benzole, and filtered through a small fat-free, tared, hardened filter paper (see Fig. 9).

All particles of free carbon are washed on to the filter with benzole, and the residue is allowed to drain dry. The filter and its contents are then transferred to a Soxhlet's extraction apparatus (similar to that shown in Fig. 6), and extracted with carbon bisulphide until all soluble matter has been dissolved out. Usually several hours are required for this operation.

The filter and contents are then dried at 100° C., cooled and weighed. The increase in weight gives the amount of free carbon in the sample, and is expressed as a percentage by weight.

COKE.

Determinations of moisture, volatile matter and ash are made on coke in the same manner as has already been described for coal.

In addition, however, the proper grading of coke for the various uses for which it is now sold necessitates grading tests to determine the amount of oversize and undersize.

To do this a representative sample of ample dimension is weighed out and is carefully sieved, first through a standard sieve of the same size mesh as the upper size limit of the particular grade, and then through a sieve of the same size mesh as the lower size limit of the grade.

The weights of coke remaining on the larger sieve and passing through the smaller sieve represent the amounts of oversize and undersize respectively in the sample, and are expressed as percentages by weight.



Fig. 9.—DETERMINATION OF FREE CARBON IN TAR.

The sample is mixed with benzole and filtered.

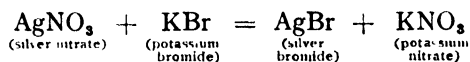
THE PHOTOGRAPHIC INDUSTRY

By H. BAINES, D.Sc., F.I.C., F.R.P.S., and D. P. WOOSLEY, B.Sc., A.I.C., A.R.P.S.

IT is only during comparatively recent years that the qualified chemist has been employed in the photographic industry. Now, however, every photographic firm of note maintains large research laboratories, and places every stage of manufacture under careful technical control. The general scheme of manufacture is tabulated in Fig. 1, and will be described in some detail.

EMULSION MANUFACTURE.

The term "photographic emulsion" is used to describe the sensitive layer on a photographic material. The emulsion consists of a suspension, in gelatin or other binding medium, of very finely divided silver halide (chloride, bromide or iodide). The halides of silver constitute the essential light-sensitive ingredient of an emulsion. They are insoluble in water and are formed when silver nitrate and alkali (potassium, sodium or ammonium) halide are mixed, the reaction being represented by the following equation:—



Of these four materials, silver nitrate, potassium bromide, and potassium nitrate are freely soluble in water whilst silver bromide is insoluble. Thus on mixing clear solutions of silver nitrate and potassium bromide, silver bromide is obtained in the solid state as a suspension of infinitesimally small crystals (each invisible to the unaided eye), which impart to the liquid a milky appearance. These crystals of silver bromide soon "coagulate," or clot, and settle to the bottom of the vessel, as a heavy, pale yellow curd.

Precipitation.

This process of formation of an insoluble substance in a dispersed form by mixing two or more solutions is known as "precipitation," and the insoluble substance formed is called the "precipitate." The precipitation of silver halide described above is used in the commercial preparation of photographic emulsions. It is

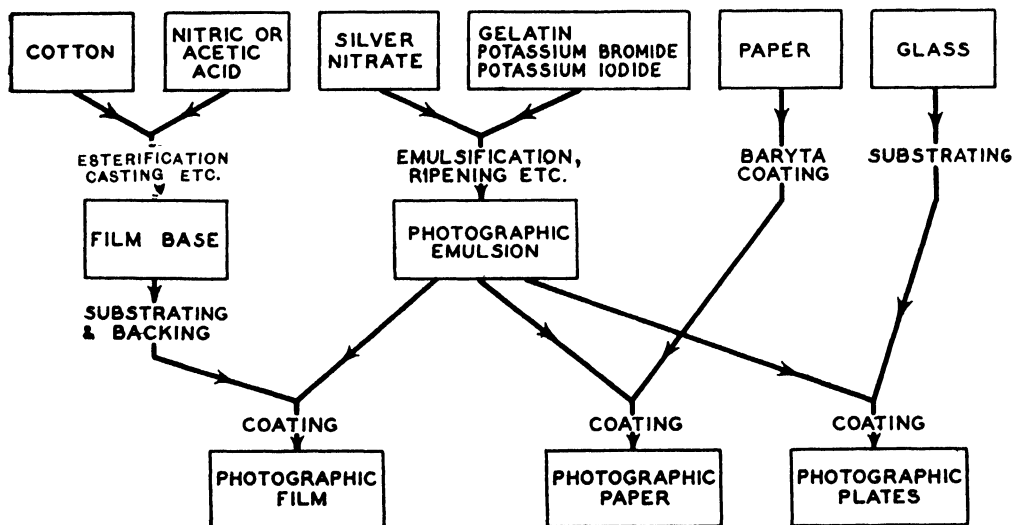


Fig. 1.—THE GENERAL SCHEME OF MANUFACTURE.

essential, however, that the small crystals or "grains" of silver halide do not coagulate and settle, and for this reason, precipitation is carried out in the presence of certain viscous, colloidal substances which may be added to one or both of the reacting solutions. Most of the vehicles which impart stability to suspensions are complex substances of animal or vegetable origin, e.g., starch, gums, glues, cellulose esters, etc. Collodion was at one time generally used as the dispersion medium of photographic emulsions, but its use is now restricted to one or two small fields. Gelatin is now almost universally employed, since it not only effectively prevents coagulation, but also imparts a high degree of sensitivity to silver halide.

Emulsification.

The process of mixing the silver nitrate and alkali halide solutions in presence of the chosen colloid is known as "emulsification." Emulsions for negative and rapid positive materials, including cine positive film and bromide paper, consist of silver bromide with 0 per cent. to 7 per cent. of silver iodide, suspended in a gelatin medium.

The emulsification must be carried out under most precise chemical and physical conditions which are different in specific details for different emulsions. All operations, from the commencement of the mixing of the silver nitrate and halide solutions must be carried out in a dark-room illuminated by non-actinic light, usually red or yellow. A carefully measured volume of a standard solution of silver nitrate, maintained at a definite temperature, is added to a gelatin solution, also at a prescribed temperature, and containing alkali halides in specified excess of equivalence to the amount of silver nitrate. The latter solution may be added in portions at definite intervals of time or during a fixed period by accurately controlled flow. In many cases, sufficient ammonia solution is added to the silver nitrate just to redissolve the brown precipitate of silver hydroxide first formed.

Ripening.

The resulting emulsion is, however, usually not sufficiently sensitive to light and in order to obtain the required "speed," the emulsion is "ripened" by

maintaining it for a definite time at a definite temperature by immersing the vessel in a thermostatically controlled water bath. During this process the grains of silver halide increase in sensitivity and in size, but decrease in number, the largest growing at the expense of the smallest. This phenomenon is known as "Ostwald ripening" and is due to the higher solution pressure of the smaller grains.

After the ripening has proceeded to the desired extent, further gelatin is admixed, and the resulting viscous emulsion is cooled until set. The jelly is next forced through a perforated silver plate to convert it into shreds, as a preliminary to the next operation

Washing.

The purpose of this washing process is to remove, by lixiviation, the excess alkali halide and the alkali nitrate formed as by-product of the reaction. These unwanted soluble compounds are completely eliminated when the emulsion shreds are kept for upwards of an hour in a canvas bag in running or frequently changed water.

The required degree of freedom from soluble salts is determined by rapid quantitative colorimetric tests applied to the effluent wash water or by a determination of the electrical conductivity of a small sample of the emulsion. After the completion of washing, the surplus water is drained from the shreds, which are then ready for a "digestion" process, if such be needed.

Digestion.

The drained shreds are melted by heat, a weighed quantity of gelatin is added and sufficient water to bring the total weight to a constant predetermined value. The temperature of the liquid emulsion is maintained at an accurately controlled level for a definite time, at the end of which period the required photographic characteristics will have been attained.

The two heat treatments, ripening and digestion, each fulfil entirely different functions in determining emulsion characteristics, slight changes in either process, or in emulsification conditions often leading to profound changes in photographic quality. The effect of a given modification in manufacture is dependent

upon the previous and subsequent history of the emulsion, and may therefore be quite different when applied to different types of emulsion. Similarly, two different modifications of a formula, each separately having a similar effect on the subsequent photographic properties, may, when *simultaneously* introduced, produce an opposite effect.

The dependence of sensitometric properties upon conditions of manufacture is thus an extremely complex relation, and it is only during recent years that photographic chemists have been able to recognise a few of the fundamental principles involved. Conditions of manufacture for each type of emulsion have to be adjusted so that not only the required speed, contrast and freedom from "chemical fog" are attained, but also the desired latitude, "graininess," grain size, resolving power, spectral sensitivity and stability towards heat treatment of the coated material.

On completion of digestion, the emulsion is cooled. The silver content is determined and adjusted to a constant value by appropriate dilution in order to correct any slight variation due to differential swelling during washing or to incidental losses during manipulation. If not required for immediate coating, the emulsion may be chilled until set, and stored in a refrigerated chamber.

Colour Sensitising.

An emulsion of silver bromide and iodide in gelatin is sensitive only to that portion of the spectrum between the ultra violet and the blue-green (3,400 A.U.—5,600 A.U.). As a consequence of this difference in spectral sensitivity between the photographic emulsion and the human eye, the relative luminosities of coloured objects photographically rendered in monochrome will differ from their corresponding visual brightnesses. For example, a lemon on a dark blue plate appears to the eye as a light object against a dark background. On the other hand, a photographic emulsion, being highly sensitive to blue and insensitive to yellow light, would reproduce the group as a dark object on a light background.

How Sensitivity is Extended Beyond the Normal Range.

Vogel discovered in 1873 that by small

additions of certain dyes to emulsions, he was able to extend the sensitivity beyond the normal range towards the red end of the spectrum. In this way emulsions dyed with corallin, for example, were rendered sensitive to green and yellow light as well as blue and ultra violet, and were known as "orthochromatic" or "isochromatic" emulsions. Further research has produced dyes which are capable of sensitising emulsions to the whole of the visible spectrum, the resulting emulsions being termed "panchromatic." Such materials in combination with suitable filters for repressing the ultra violet and blue light, possess a spectral sensitivity closely approximating to that of the human eye. They are of special value for photography in artificial light, in which red and yellow preponderate. Fig. 3 shows the spectral sensitivity of silver iodobromide; (top) unsensitised; (centre) orthochromatised; and (bottom) panchromatised.

Modern Sensitising Dyes.

Practically all modern sensitising dyes are members of the large group of unstable basic dyes known as the cyanines, which are characterised by an unsaturated chain of carbon atoms uniting two heterocyclic nuclei. Some recently discovered examples of this group of dyes possess such remarkable sensitising properties that panchromatic emulsions are marketed, whose induced sensitivity to red light is almost equal to the original sensitivity to blue. Moreover, it has been found possible to sensitise emulsions to the infra red, as shown in Fig. 4. This development has found application in medicine, entomology, microscopy, spectroscopy, astronomy, haze penetration, aerial photography and other branches of science.

Sensitising dyes may be added at any stage of emulsion manufacture, the dark-room illumination being appropriately adjusted. Panchromatic emulsion, being sensitive throughout the visible spectrum, must be handled in complete darkness, or at most, in a very dim green light of specific wavelength.

Final Treatment Before Coating.

Before it can be applied to the support, certain chemical additions have to be made to the emulsion in order to modify its physical properties. Alcohol is added to avoid froth by promoting the bursting

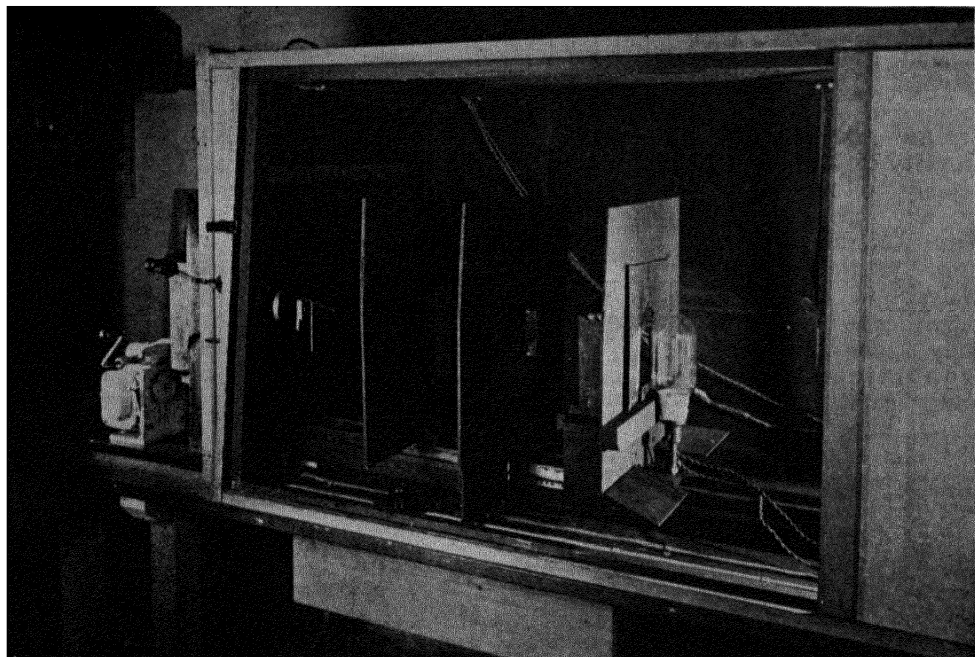


Fig. 2.—STANDARD LAMP AND SENSITOMETER FOR TESTING QUALITY OF NEGATIVE MATERIALS.

of tiny air bubbles which are sometimes entrapped during the coating process, saponin, a vegetable soap, is added to lower surface tension and thus prevent subsequent irregular or incomplete spreading of developer which would result in uneven development, and chrome alum or formalin is added because of its insolubilising action on the gelatin. The emulsion is removed from the refrigerator, melted to a convenient temperature and the required additions are made. After careful filtration the emulsion is maintained at constant temperature until its viscosity becomes stable, any deviation from the prescribed viscosity being counteracted by appropriate dilution or temperature change. It is then ready for coating on the support, at the temperature of stabilisation.

Chemical Control During Emulsion Making.

It has been pointed out that slight changes in physical conditions during emulsion making may exert a profound effect upon photographic characteristics. Similarly minute traces of impurities may exercise a highly deleterious action upon the finished product, giving rise to

“chemical fog,” loss of speed, alteration of contrast, stain, spots, etc. Accordingly all raw materials used in emulsion manufacture are of A.R. quality, and are subjected to rigid chemical analysis. In many cases their photographic effect also must be determined before they are passed for use. The photographic effect is determined either by incubation in suitable contact with photographic materials, or by making a trial batch of emulsion using the material under observation. These supplementary tests are necessitated by the fact that certain possible impurities may exert a photographic action when present in concentrations too small to be detected by the most delicate of known chemical tests.

Gelatin.

One of the most capricious of raw materials encountered by the photographic chemist is gelatin. Photographic gelatin represents the highest and most expensive grade obtainable, the standard being considerably higher, for example, than for food gelatins. Its manufacture is extremely difficult, and is only attempted by a few of the most advanced gelatin

factories. Gelatin, as has been mentioned, exerts a powerful sensitising action on silver halide, and this property cannot be reliably estimated by any chemical test. Accordingly, after preliminary analysis to avoid impurities in chemically detectable proportions, a tender sample of every batch of gelatin is tested by preparing a photographic emulsion which is subjected to the most rigid examination. The adequate testing of each batch of gelatin costs several pounds and occupies several weeks, the gelatin manufacturer reserving the bulk until a decision is reached.

Apart from the examination of raw materials, the accuracy of additions to emulsions, and the monetary value of the materials handled are of such importance that a constant check is made upon the concentration and purity of all solutions in order to detect errors in compounding.

Positive and Print-Out Emulsions.

The faster types of positive emulsion, such as are used for bromide paper and cine positive film, have been sufficiently considered above. There remain two other groups of positive materials:

- (1) Gaslight papers and lantern plates;
- (2) Self-toning and print-out papers.

The emulsions for the first group consist chiefly of silver chloride and their method of preparation differs from that of a negative emulsion only in that the washing process is usually dispensed with. Self-toning and print-out emulsions, consisting of a mixture of silver chloride and citrate may have either gelatin or cellulose nitrate (collodion) as a medium. Washing is omitted and, for the collodion emulsions, all the reagents have to be dissolved in alcohol and ether. Self-toning emulsions owe their peculiar properties to the presence of a small propor-

tion of a gold salt.

PREPARATION OF THE SUPPORT. The Casting of Film Base.

Two forms of film base exist, cellulose nitrate and cellulose acetate, of which the latter is not inflammable and is therefore known as safety base. For the manufacture of cellulose nitrate,

best quality cotton is treated with a mixture of sulphuric and nitric acids to form cellulose nitrate, which differs from gun cotton only in the degree of nitration. The nitro-cotton is washed with water until free from acid, dried, and dissolved in either acetone or a mixture of alcohol and ether. Considerable proportions of other compounds, such as camphor, are also dissolved in the solution, in order to act as plasticisers for the dried film. The solution is then led on to a gelatin-coated endless copper band on which it is passed through evaporating chambers, the dried film being reeled in lengths of 1,000 to 2,000 ft, 42 in. wide. Three thicknesses of base, are in common use, three thousandths of an inch for roll films, film packs, etc., five thousandths for cine films, and seven to eight thousandths for cut films, X-ray films, and the like.

In the preparation of safety base, the cotton is acetylated by treatment with a mixture of sulphuric and acetic acids and acetic anhydride. The washing and after treatment of the mixed cellulose acetates are essentially the same as for the nitrate, except that in place of camphor, aromatic phosphoric esters, such as triphenyl or tricresyl phosphate are employed as plasticisers, approximately in the proportion of one part of phosphate to three of cellulose acetate.

Certain dyes may be added to the nitrate or acetate dopes in order to produce tinted bases for special purposes.

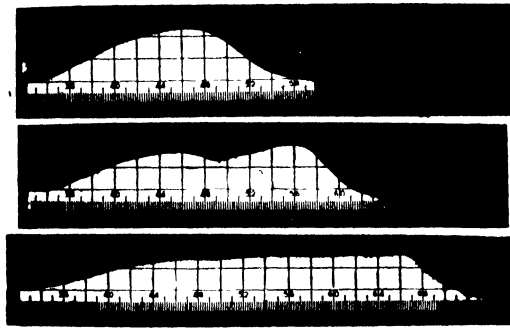


Fig. 3.—THE SPECTRAL SENSITIVITY OF SILVER IODOBROMIDE.

(Top) Unsensitized; (centre) Orthochromatized, (bottom) Panchromatized



Fig. 4.—THE SPECTRAL SENSITIVITY OF AN EMULSION SENSITIZED TO THE INFRA RED.

Substratum Coating.

If a gelatin emulsion be coated direct on to film base, its adhesion will be inadequate for normal manipulation. The emulsion layer can be readily peeled off in the dry state, and in any case would separate from the support during development. To secure good adhesion, the surface of the film base is given a preliminary treatment. It may be etched by brief immersion in alcohol-ether, the emulsion being immediately applied. An alternative method is to treat the film base with a dilute solution of gelatin in a mixture of water and acetone. The acetone dissolves part of the surface of the base and deposits it again on drying, mixed with gelatin. This intermediate layer has strong affinities for both base and emulsion with the result that excellent adhesion ensues. Fig. 6 shows a substratum coating machine in operation.

Glass.

All glass is coated in large sheets up to 3 ft. square and every sheet is washed, dried and examined with scrupulous care for blemishes and bubbles before it is passed for coating. An extremely slight regular curvature is permissible, the emulsion being coated on the concave surface.

As with film, glass is unsuitable for the direct application of gelatin emulsion and it has to be submitted to a preliminary substrating treatment. This may consist in rinsing it with a solution of chrome alum and drying, the extremely thin layer of chrome alum left on the surface being sufficient to harden the contact layer of gelatin and to cause excellent adhesion between glass and emulsion. Alternatively the glass may be coated with an extremely thin layer of hardened gelatin before applying the emulsion.

Photographic Paper Base.

Paper of only the finest quality obtainable is used as photographic base. It is made in specially equipped mills with the most rigorous scientific control from selected cotton rags and chemically prepared wood pulp. The rags are cleaned, then boiled with caustic soda solution and, with the wood pulp, are disintegrated in a beating machine until the individual fibres are completely separated. The

watery mass is engine-sized by treatment with carefully regulated quantities of potash alum and resin and is led on to an endless band of wire gauze through which the water is strained, the fibres being retained as a mat which is then passed over drying drums. The dried base is tub-sized by treatment with a very dilute hardened gelatin solution. After redrying, it is calendered by passing it between heavy granite rollers, and reeled in widths of approximately 108 inches. The length of a web is upwards of 3,000 feet, and it is slit to 42 in. or 54 in. for subsequent processes.

Baryta Coating.

The raw base is not pure white in colour, and being mechanically weak, is not often used for the direct application of emulsion. The necessary strength, stiffness, smoothness and colour are obtained by "Baryta Coating." This process consists in applying to the paper base a suspension in gelatin solution of finely divided precipitated barium sulphate, known as "baryta" or "blanc fixe."

The grain size of this precipitate is of great importance and is very carefully reproduced by strict control of the manufacturing conditions. The creamy baryta suspension is suitably tinted to give the required colour after counter-balancing the yellowness due to the gelatin or to the base. It is applied by running the paper under a roller which just dips into a trough containing the liquid. Mechanically vibrating badger-hair brushes are employed to smooth the baryta layer. The paper is then looped in festoons and dried, the whole process being repeated several times.

Finally, the paper is smoothed by calendering which imparts a highly glossy surface to the baryta layer. Such a baryta coated paper needs no further treatment with a substratum owing to the affinity between the gelatin in the baryta and emulsion layers.

APPLICATION OF THE EMULSION TO THE SUPPORT.**The Coating and Drying of Film and Paper.**

The problems attendant upon the application of photographic emulsion to film and paper are essentially similar. The emulsion, melted and treated with the coating chemicals as described earlier, is

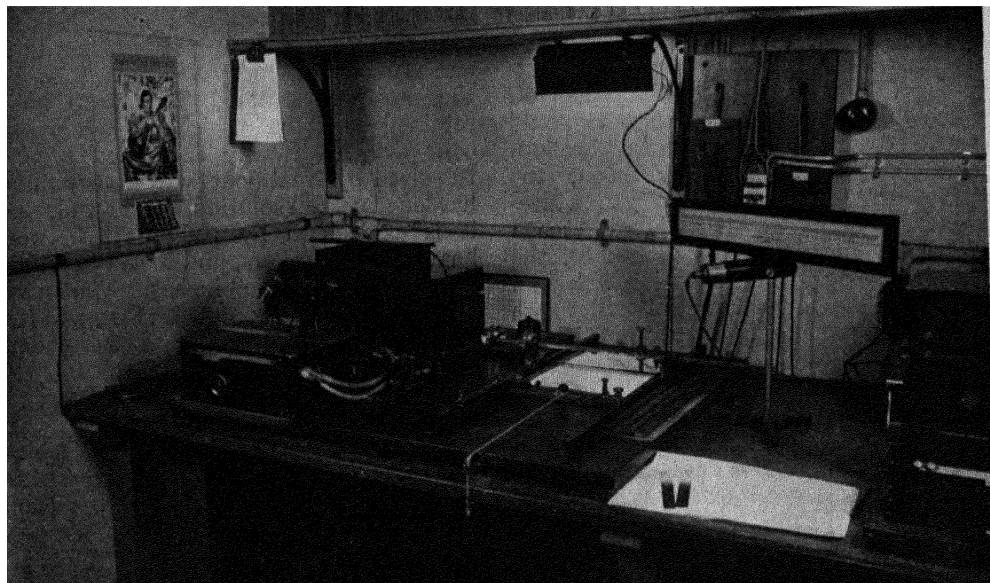


Fig. 5.—DENSITOMETER AND PLOTTER FOR RECORDING THE QUALITY OF TEST NEGATIVES.

placed in a large stainless steel vessel provided with a water jacket maintained at a constant temperature. A tube at the bottom of this vessel leads the emulsion into a water jacketed trough at the same temperature as the reservoir where a simple device maintains a constant level of emulsion. A stainless steel roller, 42 ins. long, and about 4 ins. diameter is mounted horizontally, so that its lower surface is just in contact with the surface of the liquid emulsion in the trough. The film or paper base is led down to the trough, with the substrated or baryta-coated surface respectively downwards. It is passed under the dip roller and then vertically out of the liquid emulsion, a thin layer of which adheres to the base.

After a short vertical travel the coated base is led over chilled rollers or into a chamber of refrigerated air, where the liquid emulsion quickly sets to an even layer of jelly. From the chilling chamber, the coated base passes over other rollers and is then looped in festoons by means of horizontal poles. These poles move forward slowly on endless chains and carry the loops along a tunnel called the drying track. During this process, the base, with its coating of emulsion, meets rapid currents of meticulously clean air whose humidity and temperature vary

progressively along the length of the track in a carefully controlled manner. Finally, the dry paper or film is reeled and stored in a dark room until it is required for the next process.

Modifications of the Coating Process— Nonstress Coating.

When the emulsion surface of a film or paper, coated in this manner, is lightly rubbed or pressed with a hard object, the affected portions may blacken during development without exposure to light. The resulting marks are known as "stress marks" and can be shown to be purely a surface effect since they can be removed by rubbing with wet cotton wool. It follows that if the surface is free from silver halide grains, the material would be much less liable to stress marks, and such a surface is often obtained by coating a thin layer of gelatin on the surface of the emulsion.

The gelatin or "nonstress" coating may be applied to the set emulsion immediately after emulsion coating, by leading the base under a second dip roller followed by further chilling. The path of the film between the two dip rollers is necessarily complicated, owing to the fact that the emulsion coated surface must not be brought into contact with any

guiding roller. For certain characteristics it is necessary to coat a fast emulsion over a slower one, and to apply also a nonstress coating. For this operation, a more complicated machine containing an additional coating trough may be employed.

Coating Weight.

One of the most important requirements in efficient coating is the correct adjustment of "coating weight," i.e., the quantity of silver halide coated on unit area. Coating weight is usually expressed in milligrams of silver (calculated as metal) per square decimeter, and its control is necessary not merely to avoid waste of silver, but also because photographic quality is dependent upon it. In order to produce a material which is photographically constant, it is therefore essential that coating weight be sensibly uniform throughout the length and breadth of each roll, and that it approximate very closely to a predetermined value.

Three Factors Which Affect Coating Weight.

Coating weight is influenced mainly by three factors—the silver content

of the emulsion coated, the velocity of the film travelling through the coating trough (known as coating speed), and the viscosity of the emulsion being coated. Since the first factor is made constant during emulsion making, coating weight may be brought to the correct value by adjusting the speed of the machine by means of infinitely variable gears, or by adjusting the viscosity of the emulsion, either by temperature control, or by addition of gelatin or hardening agents such as chrome alum or formalin.

In connection with viscosity adjustments it is of interest to note that the viscosity-temperature relation exhibits the phenomenon known as hysteresis. Thus, if the

temperature of a gelatin sol be rapidly changed to a new value, the viscosity pertaining to the new value is not reached until considerable time has elapsed. This complicates emulsion technique in that it is necessary to allow an emulsion to "stabilise" for periods up to one hour after change of temperature or addition of hardening agent, in order that viscosity may reach equilibrium.

Coating weight is checked chemically, by determining the silver on a known area, using cyanometric titration methods, which differ according to the type of base—film (and plate) or paper.

The Coating of Glass Plates.

Plate coating machines are built on very different lines from film and paper coating machines. The prepared plates are laid perfectly flat on endless bands which feed them edge to edge under a thin ribbon of liquid emulsion. The coated plates then pass on further chains through a chilled tunnel or in contact with a cold water surface, where the emulsion sets. At the far end, the plates are removed and placed

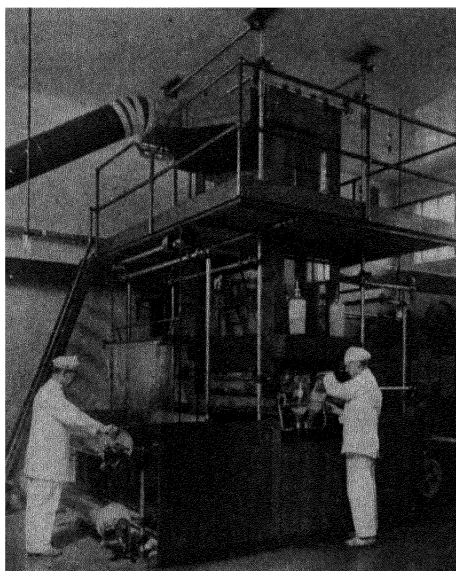


Fig. 6. A SUBSTRATUM COATING MACHINE IN OPERATION.

upright in special racks in the drying rooms. A view of a laboratory machine actually coating plates with sensitive emulsion is given in Fig. 7. This photograph was obtained under darkroom lighting conditions by the use of an Ilford Infra-Red Plate, without damage to the plates on the machine.

The Anticurl Backing of Films.

During the drying process, the thickness of the emulsion layer gradually diminishes until, in the fully dried film, it occupies only about one-tenth of its original volume. In addition to this change in the one dimension—thickness—there is also a tendency for a reduction in area to occur,

which results in bad curling with film base. To overcome this curling, the reverse side of the film is treated in such a manner that an equal tendency to contract is conferred on it.

How Cine Products are Treated.

In cine products, the back of the film is treated with special solutions of cellulose esters and certain metallic salts which not only counteract the curl, but also diminish the tendency of the film to generate charges of static electricity on unrolling the spool. Such charges are liable to cause sparks which are recorded by the emulsion as dark spots or markings.

How Roll Films are Treated.

In roll films and some other products, this anticurl treatment consists in applying to the back of the film a coating of gelatin solution of the same concentration as the emulsion.

The composition of the gelatin backing layer may be modified in two directions. A small addition of a finely divided white substance such as starch renders the dried gelatin translucent and facilitates the examination of a negative, for example, an X-ray photograph, without a diffusing medium between the light source and the negative. The starch also imparts a "matt" or rough surface to the dried film which can then be more readily retouched with a lead pencil.

Elimination of "Halation."

The gelatin may also have added to it water-soluble dyes to eliminate "halation" which would otherwise manifest itself, for example, as a blurring of the outline of branches against a sky or the

formation of haloes round the images of excessively bright objects. This spreading of light round the image of a bright object is due to the presence of a second diffuse image caused by light which has passed obliquely through the emulsion layer and suffered total reflection at the back of the film. The trouble may be eliminated by absorbing this light during its passage through the backing gelatin, by adding to the latter a dye of colour complementary to the light responsible.

Although theoretically a black backing absorbing all wavelengths is necessary, it is sufficient in practice to employ a backing absorbing the longer wavelengths in the

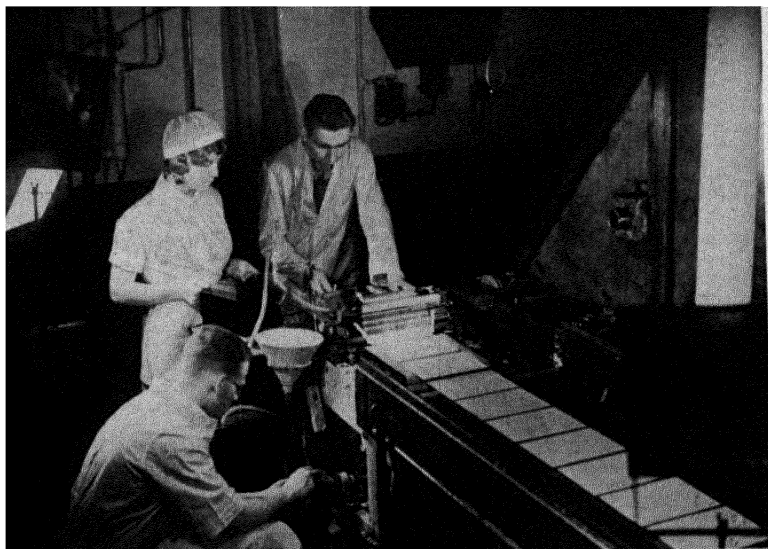


Fig 7 —A LABORATORY MACHINE COATING PLATES WITH SENSITIVE EMULSION

sensitivity range of the emulsion, since these are primarily responsible for the halation effect.

For example, a highly green sensitive film of the "chrome" type is provided with a red backing, while a red sensitive film has a grey or blue backing. These dyes, are chosen from groups forming colourless water-soluble compounds with aqueous solutions of sodium sulphite or bisulphite such as are encountered in most developing and fixing baths. Magenta or fuchsine is a simple example of such dyes and a solution of its colourless sulphite compound is well known as Schiff's reagent. Because of this property, the colour of the anti-halation backing is completely discharged during the process-

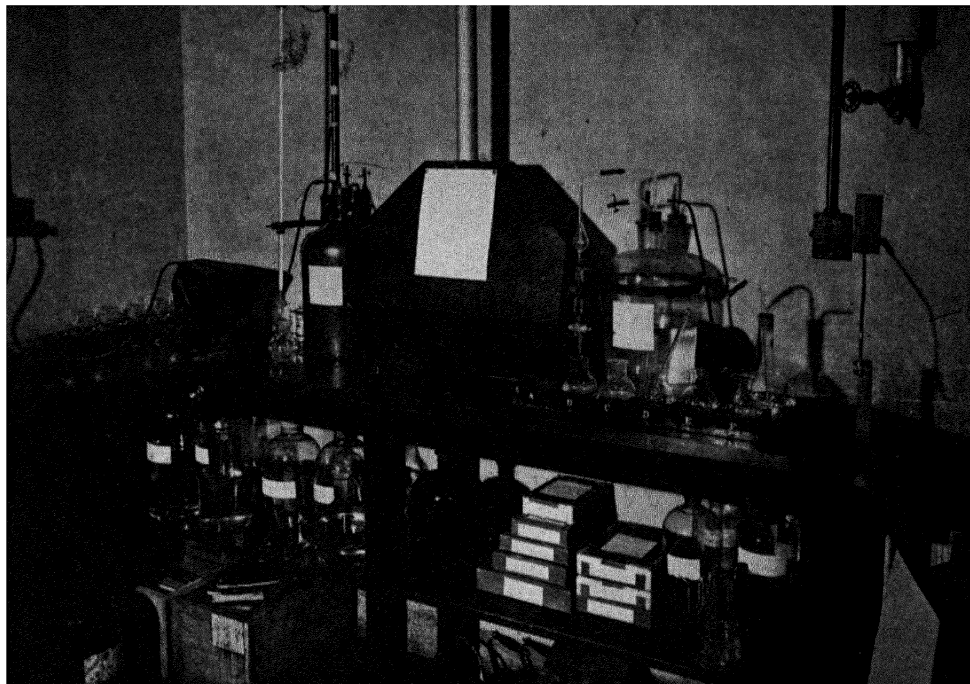


Fig. 8.—APPARATUS FOR DETERMINING THE QUANTITY OF SILVER PER UNIT AREA ON PHOTOGRAPHIC FILMS.

ing of the film, and a clear black and white negative is obtained.

CUTTING, EXAMINATION AND PACKING.

After the drying process, the film is passed through a machine which slits it to the required width and then through a guillotine which accurately cuts the narrow rolls of film into single sheets or strips. Each sheet of film is then examined with scrupulous care to ensure that it is physically perfect before being packed for sale. All these finishing processes are conducted in rooms ventilated with clean air at controlled humidities and temperatures.

PHOTOGRAPHIC TESTING.

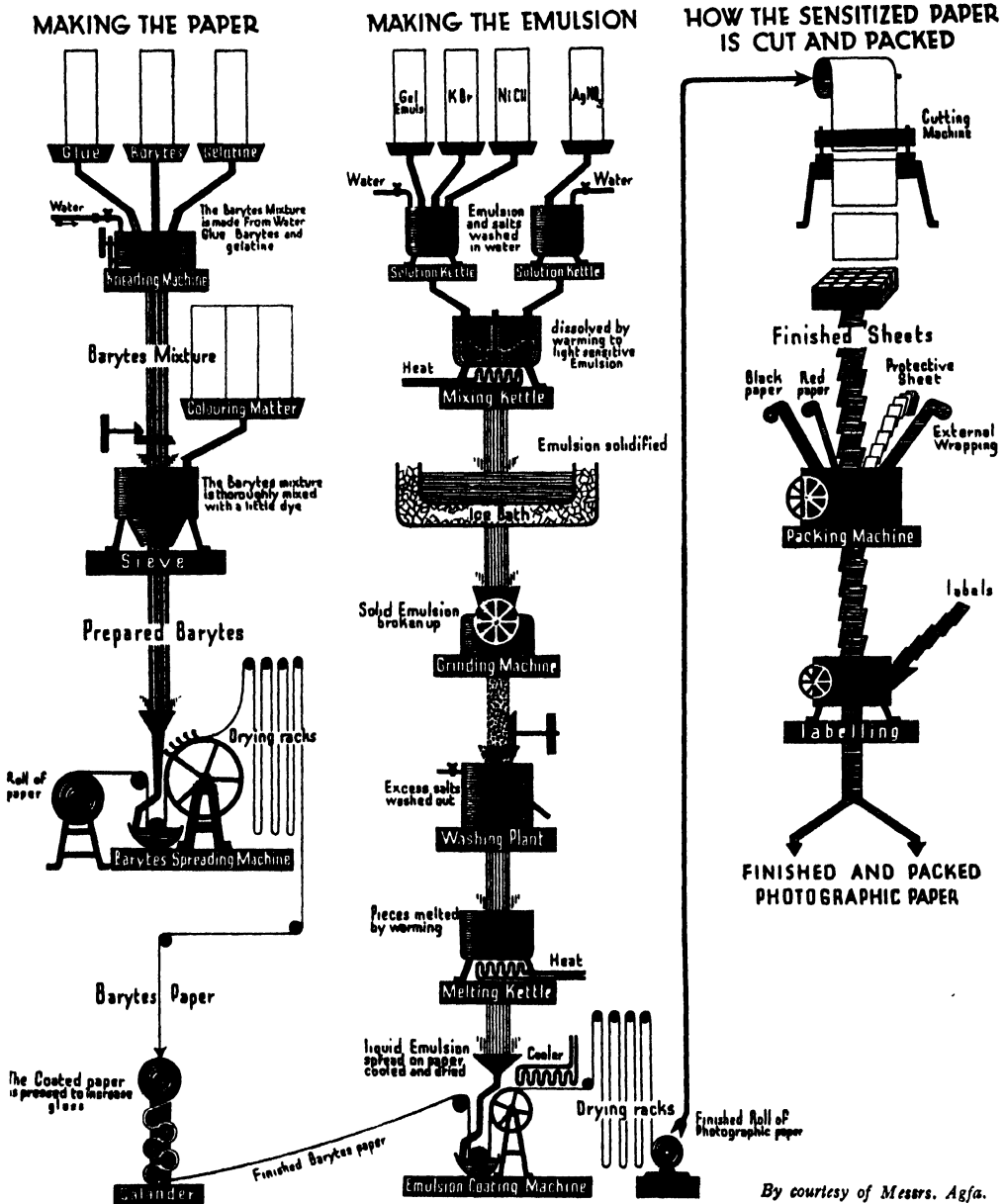
The manufacture of sensitised products is controlled photographically as well as chemically. As soon as the emulsion has been digested, before it is placed in the cold store, a sample is removed and coated on a small coating machine. The object of this test is to ensure that all the emulsion to be used on the large scale coating shall be of unimpeachable quality. Should

any defect have crept in unobserved, the faulty emulsion can be segregated for destruction. Similarly, as soon as the material is dry, large pieces of film or paper are cut out for photographic testing. In the rare event of a photographic imperfection, disposal instructions are issued to the cutting rooms. Tests are applied for fog, speed, contrast, colour sensitivity and other specialised qualities. All tests are carried out under carefully standardised conditions, such items as developer composition and temperature, exposure intensity and distance, times of exposure and development being rigidly controlled within narrow limits.

Commercial camera tests are made and the characteristics of each batch are measured sensitometrically for statistical and record purposes. In addition to the immediate photographic properties, the keeping qualities of each batch under temperate and tropical conditions are determined by prolonged normal keeping and incubation tests.

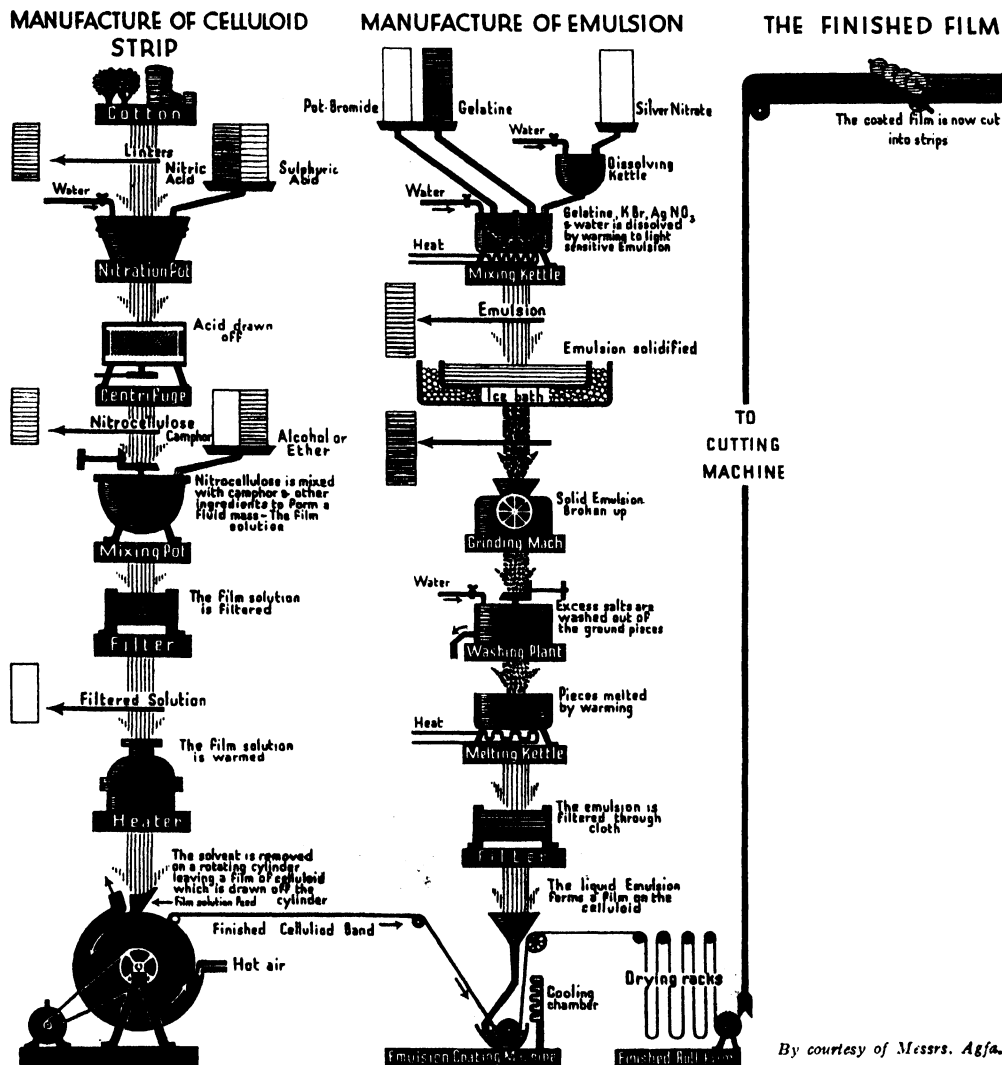
We are indebted to Messrs. Ilford, Ltd., for permission to publish the photographs which accompany this article.

THE MANUFACTURE OF PHOTOGRAPHIC



IN THE ABOVE DIAGRAM ARE SHOWN THE VARIOUS PROCESSES IN THE MANUFACTURE OF THE BARYTES PAPER AND EMULSIONS BEFORE THE FINISHED PAPER IS FINALLY FED INTO THE EMULSION COATING MACHINE. THE ROLL OF SENSITIZED PAPER THEN PASSES TO THE CUTTING MACHINE AFTER WHICH THE FINISHED SHEETS ARE PACKED AND LABELLED.

PAPER AND FILM SHOWN PICTORIALY



THE ABOVE DIAGRAM SHOWS THE STAGES IN THE MANUFACTURE OF ROLL FILM. THE PREPARED SOLUTION AFTER WARMING PASSES TO A ROTATING CYLINDER WHERE THE SOLVENT IS REMOVED LEAVING A FILM OF CELLULOID WHICH IS DRAWN OFF THE CYLINDER AND PASSES TO THE EMULSION COATING MACHINE. AFTER DRYING, THE COATED FILM PASSES TO THE CUTTING MACHINE WHERE IT IS CUT INTO STRIPS.

PRINTING INKS

PART III.—TESTING OF PIGMENTS AND DRIERS

By G. L. RIDDELL, Ph.D., A.I.C.,

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PIGMENTS.

PIGMENTS are most important components of printing inks and must be selected with care since they not only affect the working properties of an ink but also determine very largely whether or not the finished print will be satisfactory during use.

Printing ink pigments are of a number of kinds. The majority of black inks are pigmented with carbon black and may be toned, to overcome the natural brownish colour, with blue or purple pigments or dyestuffs. The pigments used for coloured inks vary in character considerably. Naturally occurring mineral colours such as siennas, ochres and umbers are used as well as synthetic inorganic colours of which chrome yellows, iron blues and zinc white are typical. Organic pigments are of two kinds, either pigment dyestuffs of which Helio fast red and the Hansa yellows are examples or lake compounds such as lake red C or methyl violet lake.

Tests which are made on printing ink pigments are usually comparative and a series of standard pigments, known to be satisfactory, are kept stored in airtight tins. Thus every new batch of dry colour received is compared, by a *standardised procedure*, with its appropriate standard. The actual methods employed in the industry vary slightly but providing a uniform procedure is followed, the results obtained are comparable and informative.

Preparation of Pigments for Testing.

In order to test pigments for a number of their properties, such as overtone, i.e., colour in thick films; undertone, i.e., colour in thin films, colour strength, ease of grinding, etc. it is necessary to make them up into an ink by grinding with a thin lithographic varnish, the same procedure being followed for both the dry colour under test and the standard sample. 0.5 gm. of the pigment is accurately weighed out on to a watch glass and a small depression made in the pile. Further weights are added to the balance pan and a thin lithographic varnish added drop by drop into the depression until balance is restored. It is impossible to give precise details of the amount of varnish which should be added to the pigment to produce a workable ink since it varies with each different pigment but in general it is about a half to one-and-a-half times the weight of dry colour.

The object of making the depression in the pile of pigment and placing the varnish therein is to prevent the watch glass being soiled so that the varnish and pigment can be removed easily and completely. The

pigment and varnish are transferred to a slab, preferably a heavy lithographic stone or alternatively a piece of heavy plate glass and after thorough mixing with a steel knife, ground with a muller.

The Muller.

The muller should be of glass, or stone and should weigh not less than 3-4 lb. so that the

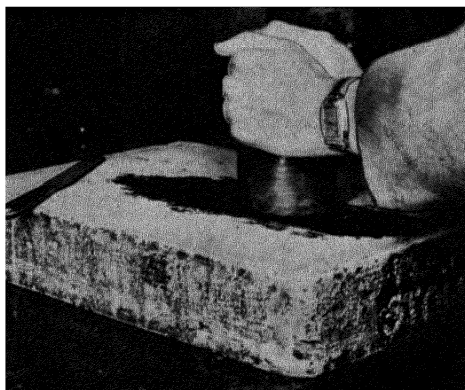


Fig. 1.—USING THE MULLER TO GRIND PIGMENT AND VARNISH.

ink can be ground with the minimum of effort. The muller is held in both hands and the ink ground with a straight up and down stroke of about 12 in. (see Fig. 1). The motion of the muller should not be circular since this results in uneven grinding. At the end of every 25 strokes the ink is scraped off the slab and muller and thoroughly mixed with the knife before being mulled for another 25 strokes. This procedure should be continued until the colour is completely mixed with the varnish and the whole is homogeneous.

In this way two prepared inks are obtained, one made with the pigment under test and the other with standard and these are used for various tests.

Ease of Grinding.

Some indication of the ease with which the pigment can be ground is obtained by counting the number of strokes of the muller required to mix thoroughly the pigment and varnish. This should, however, merely be taken as indicative, the only really reliable method being an actual practical test on an ink mill.

Undertone.

The undertone of a pigment is judged by comparing a draw-out of the ink prepared from it with a draw-out of the "standard" ink on a white hard-surfaced paper—a super-calendered printing is suitable. A draw-out is made in the following way.

A spot of the ink is placed at the top of a sheet of paper which is held firmly at the upper edge with the left hand. A broad push knife, held in the right hand and inclined towards the body and making an angle of about 60° with the paper is drawn with a steady motion down the sheet so that the ink spot is drawn out into a thin film as in Fig. 2. By exerting heavy pressure on the knife a very thin film of ink is obtained from which the undertone can be judged.

Overtone.

The overtone of a colour can be examined by making a draw-out as above but less pressure is applied to the knife so that a thicker film is obtained. A more convenient method, however, is to place a thick film of the two inks side by side on a thin colourless glass plate such as a microscope slide and to view them from the reverse side by reflected light. If the inks have the same overtone no line of demarcation between the two inks will be visible. (See "Tinctorial Strength" in a later article.)

Colour Strength.

The colour strength of the pigment is compared with the standard by reducing the made-up inks with a zinc oxide white mixing ink.

Fastness to Light.

It is important that printing inks should not fade when exposed but the accurate determination of the light fastness of inks is not an easy matter. Artificial light sources do not usually give results which are comparable with outdoor exposure and all that can be deduced

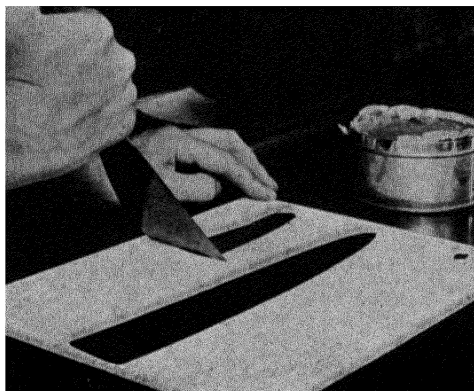


Fig. 2.—METHOD OF MAKING A DRAW-OUT FOR TESTING UNDERTONE OF A PIGMENT.

from artificial tests is that if a colour fades under the artificial conditions it will probably fade on outdoor exposure. There is no certainty that an ink which withstands artificial light will withstand sunlight. Similarly, it is not possible to say that a given number of hours of exposure to artificial light is equivalent to a given number of hours of sunlight. The method customarily employed is to make an ink from the pigment with a thin lithographic varnish and to reduce this with a known and constant amount of zinc white ink. A solid print is then made on white paper with the reduced ink which is allowed to dry and exposed to light for a given time, one half being covered with an opaque shield. A reduced ink is used since tints fade more readily than full strength colours.

The most suitable of the common sources of light is the carbon arc lamp and a

sheet of clean glass should be placed between the arc and the specimen under test. (The carbon arc under these conditions gives light which approximates to sunlight more closely than the light from the mercury arc.) Precautions should be taken that the relative humidity of the atmosphere surrounding the specimen under test is kept constant and at a normal value, about 60 per cent., since relative humidity has an important bearing on the rate of fading of colours.

Another point which should be borne in mind is that artificial light fading tests do not take into account the fading of colours induced by traces of impurities in the outside air.

Resistance to Bleeding.

It is important that the pigments used in inks should not be soluble in any materials with which the ink comes into contact. For example, the pigments used in lithographic inks must not "bleed" in water, or inks which are used for printing on paper which is later to be waxed must not contain pigments which are soluble in paraffin wax. Similarly inks may be required to resist the action of oil, greases from foodstuffs, soap, etc.

A convenient method of determining the resistance of a pigment to bleeding is to take a dried print of the ink and to place it between two sheets of plain white paper which have been heavily impregnated with the particular solvent. Half-a-dozen sheets of plain, fairly absorbent paper are placed top and bottom and the whole pile placed under a weight. After several hours the pile is examined and if the white sheets are stained the ink has bled, the number of sheets stained giving some indication of the susceptibility of the pigment to bleeding. In the case of paraffin wax and similar solvents, e.g., greases from butter, lard, cheese, etc., the pile of sheets must be placed in an air oven at about 150° F. to keep the solvent molten.

Bleeding in Soap.

Soap has a strong tendency to cause printing inks to bleed and pigments which are fast even to alkali may bleed appreciably when in contact with soap. The effect of soap on printing ink pigments may be judged by placing a dried print of the ink in contact with a soap gel or a

freshly cut piece of soap and noting any discoloration there may be of the soap. If the pigment itself is available a small portion sprinkled on top of a soap gel in a test tube will indicate whether or not it will be fast to soap. A pigment which will bleed discolours the gel throughout its thickness while a non-bleeding pigment will only stain the surface layer.

Resistance to Alkalies and Acids.

Inks are occasionally required to be fast to alkalies and acids and they are tested for this by immersing a dried print in appropriate solutions for 15 minutes and comparing it, immediately after withdrawal, with a print which has been immersed for a similar time in distilled water. For resistance to alkalies solutions of caustic soda ($\frac{1}{2}$, 1, 2, 3 and 5 per cent.) are used and 2 and 5 per cent. solutions of sulphuric acid and 5 per cent. solutions of acetic, phosphoric and chromic acids are customarily employed for testing the acidity resistance.

Effect of Heat on Pigments.

Inks which are used for tin printing are dried at elevated temperatures and the pigments used must not change colour when heated. This property is examined by rolling out an ink made from the pigment under test on a sheet of tinned iron about 4 in. $\times$ 4 in. which is cut in half. One half is placed in an air oven under similar conditions of temperature and time to those under which the ink will be used in practice. (If these conditions are not stated, 20 minutes at 120° C. can be adopted.) After the heat treatment is completed and the specimen cooled the colour of the ink film is compared with the second half of the plate and any colour change noted. It should be realised that the varnishes in the ink, particularly if cobalt driers are used, will darken slightly on heating and due allowance must be made for this.

Particle Size of Pigments.

The particle size of pigments has an important bearing on the working qualities of inks and the relative size of pigments is determined microscopically by making a dispersion of the pigment in raw linseed oil or canada balsam dissolved in xylene on a microscope slide and viewing under a $\frac{1}{8}$ -in. objective. This is described in a later article.

Oil Absorption.

The oil absorption of a pigment is defined as the smallest number of cubic centimetres of raw linseed oil required to wet completely 100 gm. of pigment. Pigments vary considerably in their oil absorption values and it is important that this should be determined since an ink with a low oil absorption value will require less oil or varnish to make an ink of a given consistency than a pigment with a higher oil absorption value.

Oil absorption values are most conveniently determined by the "rub-out" method. Ten gm. of pigment is accurately weighed out and transferred to an ink slab. Refined linseed oil is added cautiously to the pile of pigment from a burette and after each addition of oil the mixture is rubbed up *very vigorously* with a strong palette knife (Fig. 3). The pigment powder is kept in excess until the addition of one further drop of linseed oil causes the whole mass to cohere, when it will have the consistency of a stiff putty. The number of cubic centimetres of oil used is recorded and this value multiplied by ten gives the oil absorption value.

In this determination the personal factor is considerable but an operator constantly making these determinations can obtain accurate comparative results. It is important that the acid value of the oil used should be constant.

DRIERS.

As was stated on page 404 inks made on a drying oil basis have added to them small quantities of driers which have the property of accelerating, catalytically, the rate of oxidation of drying oils. Driers are salts of certain metals, usually lead, manganese, and cobalt. Cerium and vanadium compounds also have the property of increasing the rate of oxidation of drying oils but their high

cost precludes their general use in practice.

Two Classes of Driers.

Driers may be divided into two main classes (a) soluble driers and (b) paste driers. Soluble driers consist of the above-mentioned metals in the form of their resinsates, linoleates, tungates or naphthenates while the paste driers are similar to an ink in that oil-insoluble salts of these metals, usually acetates, borates, sulphates, etc., are ground into a thin lithographic varnish.

Soluble driers are made in one of two ways either by fusion or by precipitation. In the first method the oxides or acetates

of the metals are fused with rosin (in the case of the resinsates) or with hot linseed or tung oil (in the case of the linoleates or tungates). In the precipitation method the rosin or the oils are saponified with caustic soda. The sodium soaps thus formed are diluted with water and a solution of a soluble salt of the metal added. This causes the precipitation of the lead, manganese or cobalt

compound which is filtered, washed and dried.

Cobalt is the most powerful of the driers and a mixture of lead and manganese is more effective than either separately. An ink film dried with cobalt rapidly forms a surface skin while the remainder of the film beneath dries slowly. Lead on the other hand dries the ink film more uniformly throughout its thickness. It is the metallic radicle which primarily controls the degree of drying obtained although the form in which the metal is present is of some importance. Another important factor is the degree of dispersion of the drier in the ink — the higher the degree of dispersion the greater the drying effect.

Driers are usually examined for their

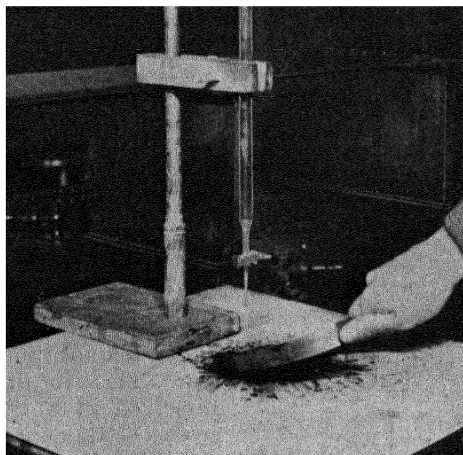


Fig. 3.—TESTING OIL ABSORPTION OF PIGMENT.
Ten gm. of pigment is rubbed up with measured volume of linseed oil.

metal content and the following methods will be found to be satisfactory.

Soluble Driers.

A known quantity of the drier is boiled with turpentine substitute until solution is effected. The hot solution is extracted several times in a separatory funnel with a hot 10 per cent. solution of nitric acid. The acid extract, in which are dissolved the metals, is retained and used for the estimation of the manganese, lead and cobalt.

Paste Driers.

A quantity of the drier is dissolved in turpentine substitute and centrifuged to separate the insoluble portion (the metallic salts). This operation is repeated about three times and the various fractions collected. The insoluble portion is washed with ether, dried and then analysed by the usual analytical procedure. The soluble portion is treated in a manner similar to that described for the soluble driers.

Estimation of Manganese.

An aliquot portion of the acid extract prepared as above is evaporated to dryness and dissolved in dilute sulphuric acid, filtered and washed with hot dilute sulphuric acid. For every estimated 50 mg. of manganese present in the filtrate 2.5 gm. of zinc sulphate and 0.5 gm. of potassium bromate are added. (The addition of zinc sulphate prevents the precipitation of iron.) The mixture is boiled for 5 to 10 minutes, the manganese being precipitated as an hydrated oxide which is filtered off and washed with hot water. The precipitate together with the filter paper is then transferred to a crucible, ashed in the usual way and finally a few drops of concentrated sulphuric acid added and taken down to dryness twice. The precipitate is weighed as manganese sulphate (MnSO_4) and the percentage of manganese in the original drier calculated.

Traces of Manganese.

The preceding method is not suitable for the estimation of small quantities of manganese which is done colorimetrically. To the nitric acid solution a small quantity of silver nitrate and ammonium persulphate is added. The mixture is boiled and

the manganese salts thus converted to ammonium permanganate which being pink in colour can be estimated colorimetrically.

Estimation of Lead.

An aliquot portion of the nitric acid extract is placed in a silica dish or large crucible and evaporated to dryness. A few c.c. of concentrated sulphuric acid are added to the cold residue and the mixture heated until dense white fumes are evolved when it is allowed to cool and washed into a beaker with about 100 c.c. of cold water. The precipitate of lead sulphate is allowed to stand for two hours and then filtered through a Gooch crucible and washed twice with approximately normal sulphuric acid and finally with alcohol until free from acid. The precipitate is then heated to constant weight and weighed as lead sulphate. The percentage of lead in the original drier can then be calculated.

Lead, if present, usually occurs in large quantities but traces may be estimated colorimetrically as lead sulphide.

Estimation of Cobalt.

An aliquot portion of the extract is evaporated to dryness and the residue dissolved in a 25 per cent. solution of hydrochloric acid. If iron is present, the solution is extracted with ether to remove the iron as ferric chloride.

Cobalt is precipitated by α -nitroso β -naphthol in acetic acid and the following solution is required, 2 gm. of α -nitroso β -naphthol dissolved in 75 c.c. of glacial acetic acid and 75 c.c. of water added. For every milligram of cobalt (estimated) 1.5 c.c. of this solution is added to the hydrochloric acid solution. The mixture is heated on the water bath until the precipitate coagulates (about one hour), and the solution is then filtered. The precipitate is washed several times with hot dilute acetic acid, dried, transferred to a crucible and ashed. The ash may be heated to constant weight and the cobalt weighed as Co_2O_3 , or better, it is converted to CoSO_4 by heating with a few drops of concentrated sulphuric acid, the excess acid being expelled by heat and the crucible and contents brought to constant weight by heating at not more than a dull red heat.

THE THREE HORMONES

INSULIN, ADRENALINE, AND PITUITARY (POSTERIOR LOBE) EXTRACT

By NOEL L. ALLPORT, A.I.C.,

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Introduction.

THE hormones are physiologically active substances with specific functions secreted by animal glands or by other specialised tissues. They may be regarded as the controlling factors responsible for the maintenance of metabolic balance. The study of these special glands and the hormones which they produce is termed endocrinology; a subject still in its infancy, which promises to revolutionise therapeutical practice.

The word "hormone" was first suggested by Starling in 1906 to describe the substance secretin, which he and Bayliss had discovered in 1902. This substance is produced by the walls of the intestine when acted upon by acid, and circulates in the blood to the pancreas, which is thereby stimulated to produce its alkaline juices. Thus a hormone may be defined as a chemical substance produced by certain parts of an organism specialised for its synthesis, and carried to distant parts which it affects for the good of the body as a whole.

The growth of plants as well as animals is regulated by hormones. The recent researches conducted by F. A. F. C. Went have proved that a specific growth-controlling substance is produced near the tip of root or shoot and diffuses through the tissues. By standing the amputated tips of shoots on blocks of agar he was able to collect this growth regulator as it diffused out of the cut end, and showed that it produced its effects when the agar block was transferred to the upper side of another amputated shoot. The hormone has been named auxine.

INSULIN.

Long before the discovery of insulin it had been known that if the pancreas be

removed from an animal the body is no longer capable of regulating the intake of sugar. When starchy foods are digested glucose is produced and it is essential to the health of the human organism that the concentration of this sugar in the blood should be just about 0.1 per cent., excepting for a short period following a meal when it may rise temporarily to 0.15 per cent. Should the pancreas fail in this function the concentration of sugar in the blood increases until it overflows into the urine and results in serious pathological symptoms characteristic of the disease called diabetes mellitus. In 1922, F. G. Banting and C. H. Best extracted from the pancreas the substance responsible for effecting this delicate sugar control which they called "insulin," in allusion to the fact that it is derived from the pancreatic tissues known as the islets of Langerhans.

Isolation of Insulin.

The pancreas, derived from oxen, pigs, sheep, or sometimes from fishes, is dissected and frozen as soon as possible after removal from the animal in order to arrest destruction of the hormone by enzymes. The glands are minced and the insulin liberated from the material by acidifying with dilute sulphuric acid until the reaction of the mixture is equal to pH 2.5. The mixture is extracted with 65 per cent. alcohol, the alcoholic extract clarified by cooling to -5°C . and centrifuging; the clear supernatant extract is concentrated to one-tenth of its volume by distilling under reduced pressure, the liquid is filtered and the proteins, with the insulin, are precipitated by treatment with ammonium sulphate at pH 5. The solids, after being separated by centrifuging, are dissolved in a mixture of dilute sulphuric acid and alcohol and the

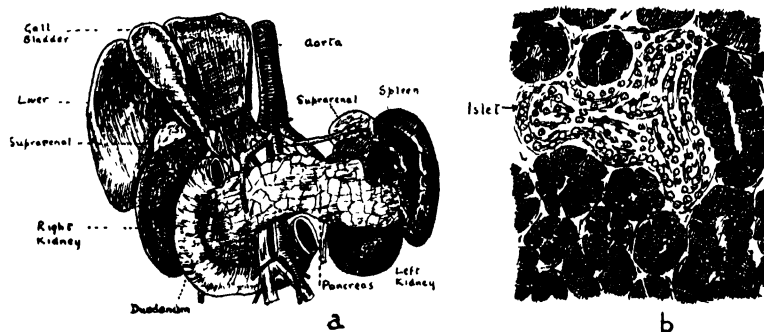


Fig. 1.—(a) THE PANCREAS AND SUPRARENAL GLANDS (b) DIAGRAMMATIC REPRESENTATION OF A STAINED SECTION OF THE PANCREAS HIGHLY MAGNIFIED, SHOWING THE ISLETS OF LANGERHANS.

international standard, is a quantity of dry soluble insulin hydrochloride, prepared and kept on behalf of the Health Organisation of the League of Nations in the National Institute for Medical Research, Hampstead, London. The unit is taken as

reaction of the solution is carefully adjusted to pH 5.2, the iso-electric point of insulin. The hormone precipitates and is thus separated from all proteins which precipitate above or below pH 5.2. The crude insulin is collected, washed, dissolved in water and precipitated as the picrate, which is separated, washed, and dissolved in a 2.7 per cent. solution of hydrochloric acid in 75 per cent. alcohol. On adding acetone to this solution, insulin hydrochloride separates and is then collected by centrifuging, and dried. There are various methods of purifying the product thus obtained and, by a somewhat complicated process, insulin can finally be obtained in crystalline form which is highly active.

Properties of Insulin.

Insulin is sparingly soluble in water at its iso-electric point (pH 5.2) but readily soluble in water that is approximately neutral (pH 7.0). It is precipitated from aqueous solution by half saturation with ammonium sulphate and sodium chloride, and also by picric acid, phosphotungstic acid and trichloroacetic acid. It is almost completely destroyed by decinormal sodium hydroxide at 37° C. in 1½ hours. In neutral solution it is decomposed at 100° C. in 10 minutes, but is more stable in decinormal acid. Its structure probably resembles that of the proteins since it is readily destroyed by the enzymes pepsin and trypsin. It does not contain phosphorus, but gives a well-marked reaction for organic sulphur.

Unit of Insulin.

The standard preparation, which is an

the amount of activity contained in 0.125 mg. of this standard, but this value may be varied from time to time.

Assay of Insulin.

Insulin is assayed by observing its effect on the sugar concentration in the blood of rabbits or by observation of the rate of convulsing in mice. If a rabbit is kept for 20 hours without food the content of sugar in its blood will be about 0.11 per cent. and the administration of a moderate dose of insulin will cause a temporary fall to about 0.05 per cent., or even less, the value reaching its minimum in about two hours.

To conduct the test, 20 rabbits are weighed and divided into two similar groups. After being kept for 22 hours without food, samples of blood are withdrawn from the ear vein of each rabbit and the percentage of blood sugar is determined. The rabbits of the first group are each injected subcutaneously with 0.5 unit of standard insulin per kilogram body weight, and each rabbit of the second group is similarly treated with a dose of the sample under test which is expected to be approximately equal to that of the standard administered to the first group. Blood is collected from each animal at hourly intervals for five hours after the injection, and the mean percentage of blood sugar in the five samples is determined for each rabbit. The difference between the original percentage of sugar in the blood and the mean percentage during five hours after injection gives the average fall for each animal which is expressed as a percentage of the original value and is called the percentage blood

sugar reduction. The whole test is repeated three days later, using the same animals, but with the groups reversed so that the rabbits which originally received the standard insulin are now injected with the sample and vice versa.

Calculation of Results.

To calculate the results the sum of the numbers for the percentage blood sugar reduction for each rabbit due to the sample is divided by the corresponding sum due to the standard and the result multiplied by 100. This number represents the percentage activity of the sample being tested in terms of the standard preparation. This test is repeated a number of times for every batch of insulin; a final value only being accepted when the dose has been successfully adjusted to give a result equal to that of the standard.

Several methods have been devised for determining the percentage of glucose in the blood, but space will not permit of their description. All the processes depend upon preliminary removal of the proteins followed by measurement of the reducing power of the protein-free filtrate. In making the determinations it is only necessary to use about 1 ml. of blood, while some of the methods are capable of giving accurate results with even smaller samples.

Pharmacy of Insulin.

It is not certain that insulin can effect a lasting cure of diabetes mellitus but, when injected subcutaneously into the patient, it corrects the sugar balance and offers complete relief from the distressing symptoms of the disease. Treatment is usually combined with a regulated diet freed as far as possible from carbohydrates whereby only small doses of insulin need to be administered. Thus a patient suffering from diabetes of moderate severity may inject himself with 10 units

twice a day.

A sterile aqueous solution of insulin hydrochloride containing 20 units per millilitre is usually employed for injection. It is important that this solution should have an acid reaction within the range pH 3 to pH 4 and, if packed in sealed vials

containing more than one dose, an antiseptic such as phenol or cresol should be present.

The remarkable results achieved by insulin treatment are generally known and need not be described at length. Apart from completely alleviating the discomforts resulting from diabetes of average severity, the administration of insulin to patients in an apparently hopeless condition of coma results in complete recovery.

ADRENALINE.

This hormone, which is the substance responsible for regulating the blood pressure, is secreted by the suprarenal glands which are situated just above the kidneys. The chemical constitution is known and most of the material used to-day is prepared synthetically according to the scheme illustrated diagrammatically in Fig. 2.

Properties of Adrenaline.

Adrenaline is a basic substance sparingly soluble in water, but readily dissolved by dilute acids. It occurs as a pale buff-coloured powder. It is insoluble in alcohol and in ether, but is dissolved by an aqueous solution of sodium hydroxide but not by solution of ammonia.

Colour Reaction of Adrenaline.

When a few drops of ferric chloride solution are added to a faintly acid solution of adrenaline a brilliant emerald green colour is produced; if to this green liquid a slight excess of sodium bicarbonate is

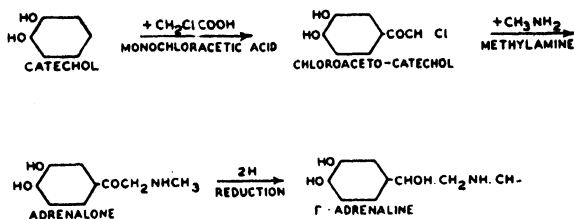


Fig. 2.—THE SYNTHESIS OF ADRENALINE FROM CATECHOL.

The adrenaline produced by the synthesis is optically inactive and possesses considerably less physiological activity than the natural product and is called racemic adrenaline. The removal of the less active dextro-base can be effected by crystallisation of the lævo-tartrates, the lævo-adrenaline salt being the more sparingly soluble.

added the colour changes first to blue and then to red.

Colorimetric Determination of Adrenaline.

A useful method of assaying samples of adrenaline, which depends upon the measurement of the colour produced when a known weight of the sample is oxidised under standard conditions, has been devised by J. H. Barker, C. J. Eastland, and N. Evers. The oxidising reagent consists of a freshly prepared aqueous solution containing 0.2 per cent. of potassium persulphate, 1.0 per cent. of sodium chloride, 0.937 per cent. of sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and 0.239 per cent. of disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$). The reaction of this solution should be pH 5.5. One ml. of this reagent is added to 1 ml. of a 0.01 per cent. solution in very weak hydrochloric acid of the sample of adrenaline to be tested and the mixture maintained at 22° C. for 30 minutes. The solution is now transferred to a 1 cm. glass cell and the colour measured in a Lovibond Tintometer (see article on Colour, Vol. 1, page 203). When treated in this manner 0.1 mg. of adrenaline will produce a colour in which the red component is equal to 10.0 Lovibond units; under these conditions the intensity of the red colour is directly proportional to the quantity of hormone present.

Therapeutic Uses of Adrenaline.

When a solution of adrenaline hydrochloride is injected hypodermically it constricts the blood vessels in the neighbourhood of the site of injection and, when mixed with an anæsthetic such as cocaine or procaine, it prevents the medicament from being carried away by the blood stream and thus ensures a prolonged localised effect. It also minimises the bleeding caused by the subsequent operation. It is also useful for relieving the spasmodic attacks of asthma since it dilates the contracted muscles of the bronchioles and enlarges the airway into the lungs. Adrenaline is an important restorative during surgical operations when as a result of respiratory failure or of a large fall in blood pressure, the heart ceases to beat. In such cases adrenaline is injected directly into the heart which can then be induced to restart by massaging. The drug is also occasionally employed for

dilating the pupils, although its mydriatic potency is not nearly so great as that of the alkaloids of belladonna.

PITUITARY (POSTERIOR LOBE) EXTRACT.

The pituitary body is situated in the hollow of the bony partition which separates the brain from the eyes, nose, and mouth (see Fig. 3A). Reference to Fig. 3 will show that the pituitary consists of two lobes surrounded by supporting tissue; if the gland is frozen and the tissue covering the under surface is cut away the lobes readily separate.

Preparation of Extract of the Posterior Lobe.

The glands are usually obtained from oxen, although the pituitary derived from other mammals is equally effective. In order to avoid loss of the physiological potency due to the action of enzymes, the pituitary bodies are frozen immediately after removal from the freshly killed animal. The posterior lobes are separated and extracted at a temperature of 10° C. with water slightly acidified with acetic acid so that the pH of the liquid lies between 3 and 4. The separated aqueous extract is then rapidly heated to the boiling point in order to precipitate as much protein material as possible. It is essential that the extract should be heated as quickly as possible, particularly between 20° C. and 55° C., which is the most favourable range of temperature for the destructive activity of enzymes. The filtered extract should be standardised so that it contains 10 units per ml.

Unit for Pituitary (Posterior Lobe).

The unit adopted for international use is the amount of activity contained in 0.5 mg. of a certain specimen of dry posterior lobe which has been freed from fat by extraction with acetone. If all possible care has been taken to avert loss of activity, a preparation containing 10 units per ml. can be made by extracting 2.5 gm. of the fresh posterior lobe with 100 ml. of acidulated water.

Therapeutic Use of Posterior Lobe Extract.

The therapeutic properties of this medicament are manifested in the following different ways:—

(1) The oxytocic property which is the

stimulant effect on the muscle of the uterus.

(2) The pressor effect, or power to raise the blood pressure by stimulation of the muscles of the blood vessels ;

(3) The anti-diuretic property by which the excretion of urine is delayed ;

(4) The power to increase intestinal movement.

The oxytocic property is probably the most important since posterior lobe extract is extensively employed in obstetric practice in order to induce rapid contraction of the uterus after childbirth and thereby arrest post-partum hæmorrhage. It is sometimes used during the actual birth to augment the natural contractions when these are insufficient to effect delivery. Its oxytocic property is allied to that of ergot (see Vol. III, page 1076), but it differs from the latter drug since it acts more quickly, although the action is more transient.

When pituitary extract is injected into the blood stream a rise of blood pressure ensues and this property is useful to counteract the effect of surgical shock following operations.

The anti-diuretic property is useful for treating diabetes insipidus. This form of diabetes has no relation to diabetes mellitus, which has been mentioned in connection with insulin. Those afflicted with diabetes insipidus suffer from terrible thirst as a result of excessive excretion of water by the kidneys. The disease can be controlled, but not cured, by administration of pituitary (posterior lobe) extract.

The action of this drug on the intestinal movements is useful for treating post-operative ileus, a condition which often follows abdominal operations in which the intestines stagnate until their functions

are restarted by a dose of pituitary extract.

Chemistry of Posterior Lobe Extract.

There are at least two physiologically active principles, one of which is termed oxytocin and the other vasopressin. A partial separation of these two hormones has been accomplished.

Separation of Oxytocin.

The ordinary extract is concentrated at a low temperature and the total active material salted out by adding ammonium sulphate. The precipitate is collected, pressed, dried, powdered and extracted with glacial acetic acid. The acid extract is treated with ether and with petroleum ether in succession, and the precipitated active material is collected and dried. The dry material is dissolved in 98 per cent. acetic acid at 40° C. and again precipitated by adding ether ; the precipitate is collected and dried, and the process repeated on the dried material. The two filtrates, which

contain much oxytocic activity but only have a slight pressor effect, are combined and treated with water and then with petroleum ether. A fine mist is thrown down which gradually settles out as a gummy precipitate which is then dissolved in water and filtered free from fat. This solution contains a considerable preponderance of oxytocin with very little vasopressin.

Separation of Vasopressin.

The two precipitates formed by adding ether to the solution of the mixed hormones in 98 per cent. acetic acid are again dissolved in 98 per cent. acetic acid and precipitated once more by adding acetone ;

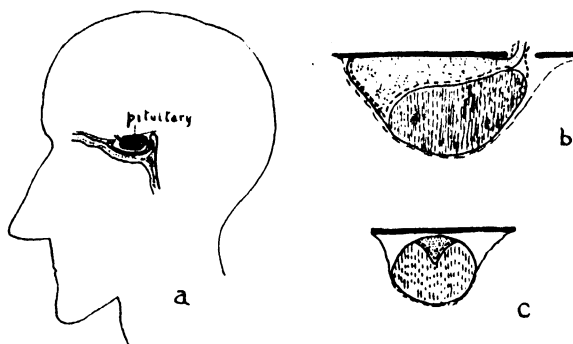


Fig. 3.—THE PITUITARY BODY.

(a) The position of the organ in the head. (b) Longitudinal section through gland ; the dotted area shows the posterior lobe surrounded by the pars intermedia indicated by the broken line ; the stippled portion is the anterior lobe and the thick upper surface is a flat fibrous piece of supporting tissue with a round orifice for the passage of the stalk which is entire with the posterior lobe and connects with the tuber cinereum. (c) Cross section through the middle of the gland.

further precipitates can be obtained from the filtrate by adding successive portions of ether. The successive precipitates which form are found to embody increasing activity with a decreasing oxytocic property. By a process of fractional precipitation it is possible to obtain a product having 10 times more pressor than oxytocic activity and possessing about 80 times the pressor potency of the international standard pituitary powder.

Standardisation of Posterior Lobe Extract.

Standardisation may be made by biological methods with reference to either the oxytocic, pressor, or anti-diuretic activity of the drug. There is not space to describe these in detail but the process for determining the oxytocic activity relative to that of the international standard follows on similar lines to that already described for the biological assay of ergot (see Vol. III, page 1079). The apparatus used is the same as that depicted in Fig. 4 on page 1078, excepting that only one bath containing Ringer's solution is necessary. The method depends upon comparing the dose of the sample which will produce a contraction of a strip of the excised uterus of the guinea pig, equal to that induced by a known quantity of the standard extract.

Measurement of the Pressor Effect.

The capacity of pituitary extract to raise the blood pressure is determined by observations on cats. The animal is anaesthetised and the spinal cord exposed and cut just behind the skull and the brain destroyed with a probe. The lungs are inflated artificially and the circulation of the blood then continues as during life. The general arterial blood pressure is recorded on a moving drum of smoked paper by connecting a small tube to a mercury manometer and inserting the other end into one of the arteries. The doses of pituitary extract are injected into

one of the veins and the sudden rise of blood pressure is automatically recorded. In this way comparisons may be made of the potency of two extracts by observing the doses of each which must be injected to produce the same rise of blood pressure.

Measurement of the Anti-diuretic Potency.

The anti-diuretic potency is compared with that of the standard pituitary by giving each rat of a group a measured quantity of water by means of a stomach tube followed by a dose of the sample. At the same time the individuals of another group receive a similar amount of water and a dose of the standard extract. The average rate of excretion of the water in each group is then observed and the experiment is repeated with varying doses until the average time of delay produced by sample and standard is the same; the potency is then assumed to be proportional to the dose. It is important that the groups be reversed in successive observations so that both sample and standard are administered at different times to all the animals employed in the test.

Future Developments.

The three hormones which have been briefly discussed constitute but a fraction of those now discovered. While it is obvious that future advances in endocrinology will certainly modify the practice of therapeutics, it should not be concluded that the use of the vegetable, mineral, and synthetic organic drugs will be supplanted. The employment of the hormones is tending to offer an almost illimitable expansion to the possibilities of medical treatment rather than to modify the successful application of the ordinary medicaments. Thus there is every hope that other distressing diseases, which hitherto have defied all the efforts of the physicians, will be finally vanquished by future developments in the science of endocrinology.

PLASTIC COMPOSITIONS FROM FUSIBLE RESINS

By H. COURTNEY BRYSON

WHEN moulded compositions first began to be used about 30 years ago, they were exclusively produced by the admixture of fusible gums, chiefly natural bitumens and coal tar pitch with fillers such as asbestos or mineral powder. The term moulding then signified electrical moulded insulator.

The Raw Materials.

Before beginning a description of typical modern methods of moulding fusible resins, it is necessary to survey the raw materials, viz., the binders and fillers. A small selection is given on page 1484.

Fibrous fillers toughen and strengthen the product; powdered fillers produce a good finish, lessen the cost, harden the surface and modify the product in various minor ways.

Suitability and Behaviour of Fillers.

It is quite obvious that different fibrous fillers will produce a difference in the finished article. A powdered filler exerts a similar influence. The suitability and the behaviour of any filler will depend on its chemical nature, its specific gravity, its molecular state (amorphous or crystalline), the size of its particles, its volume-surface ratio and the nature of the surface of its particles (e.g.,

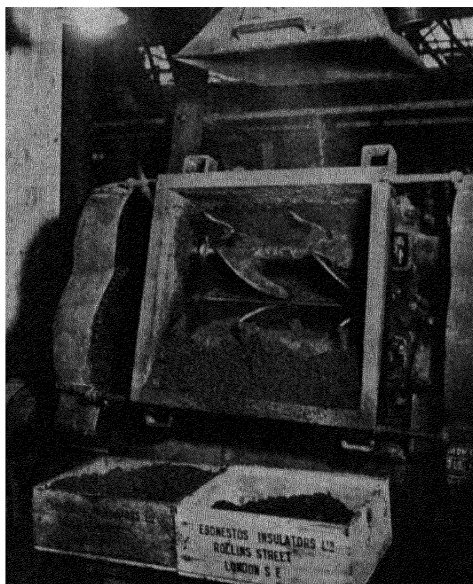
whether the binder wets the pigment or not). In certain cases even its colour, apart from æsthetical considerations, may exert an influence. Tests for fineness of pigments have been described under "Paints and Varnishes." The difference between a pigment for a paint and a filler for a plastic is one of degree and not of kind.

Processes of Manufacture.

There is much diversity in the method of manufacture of moulded articles from fusible resins. There are three methods of mixing three different types of press, three different designs of moulds, and two different modes of operation. It is possible to use any one of the given factors with any of the others, thus giving a total of 54 different processes. Actually, of course, the manufacturer never has this enormous choice. He is limited by the class of material and the shape of the article.

Method Used in Rubber and Gramophone Trades.

The oldest method of mixing and the one still used in the rubber and gramophone trades consists in compounding the various ingredients together on a pair of horizontal, heated, steel rolls, similar to those



Ebonestos Insulators, Ltd.
Fig. 1.—EMPTYING OUT THE MIXED MATERIAL FROM A UNIVERSAL MASTICATOR.

The blades are put into "reverse" so that they revolve away from, instead of towards, each other.

RAW MATERIALS.**Binders.**

NATURAL ORIGIN		ARTIFICIAL ORIGIN	
<i>Animal.</i>	<i>Vegetable</i>	<i>Mineral</i>	<i>By Products.</i>
Lac in all its modifications.	Gum congo	Asphalts, e g ,	Coal-tar pitch
Shellac	Gum copal	Gilsonite.	Petroleum pitch.
Button lac	Colophony	Manjak	Stearine pitch.
Ruby lac	Dammar	Trinidad pitch	
Garnet lac	Oils, e g ,	Sulphur	
Seed lac.	Linseed,		
	Tung, Castor		

Waxes and non-drying oils are also used Their function is chiefly to act as lubricants. They are not, therefore, included

Fillers.

FIBROUS.		POWDERED.	
Asbestos : white fibre.	Wood meal.	Gypsum.	Chalk.
Blue (acid proof)	Shoddy.	Barytes.	Mica.
Cotton flock.	Silk waste.	Slate dust.	Colouring matter.

shown in Fig. 2, which revolve towards each other at different rates, thus exerting a tearing action on the material. At the beginning the rolls are set close together and the binding material thrown on where it immediately melts.

As mixing proceeds and the fillers are added, the rollers are adjusted so that there is always a little heap of material along their whole length. Friction tends to overheat the material. In order to prevent this, cold water is often circulated through the rolls towards the end of the mixing.

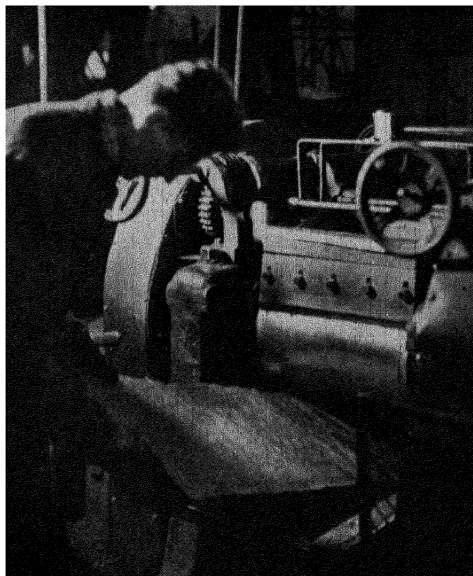
During the compounding, the composition generally sticks to the faster moving roll forming a continuous band round it and is occasionally stripped and thrown back again to facilitate mixing. When all the fillers are incorporated and the material is homogeneous, it is either scraped off and passed through cooled blanking rolls to produce a sheet, or if of a more rubber-like nature it may be peeled from the mixing mills as a smooth sheet and laid on racks till required.

method of mixing depends on incorporating the binders and fillers in a gas- or steam-heated masticator, such as a dough mixer. This consists of a jacketed or unjacketed rectangular trough wherein are two blades revolving at different speeds. These blades are plainly shown in Fig. 1. Their exact design varies according to the material which is to be treated. The binding materials are first added to the hot mixer and, when these are thoroughly melted and homogeneous, first the fibrous fillers and then the powdered fillers are slowly added. Occasionally during the mixing, the blades are put on the reverse

by means of a clutch so that they revolve away from instead of towards each other. This ensures absolutely thorough mixing.

Resins Dissolved in a Solvent.

If instead of melting by means of heat, the resins are first dissolved in a solvent and then mixed with the fillers the solvent being afterwards driven off, the latter acts as a vehicle transporting the resins right into the substance of the fibres so that a kind of alloy is formed, giving more intimate and some-



Edonestos Insulators, Ltd.
Fig 2 —To PRODUCE A MORE OR LESS HARD SHEET, THE MIXED MATERIAL IS PASSED THROUGH A PAIR OF STEEL ROLLERS.

Melting Resins by Means of Heat.

The second

times less bulky mixtures. This method is largely used in making up cellulose acetate moulding powders.

Types of Moulds.

Of the three available types of moulds—closed, semi-closed, and open or flash moulds—the former is very seldom used for permanently fusible resins largely on account of expense; the second is occasionally used, while the last type is in general use. In this connection it should be noted that in mould design care is necessary to ensure that the articles may be quickly and easily ejected, this point being the one where the greatest number of mistakes is made.

Multiple Moulds.

Multiple moulds are often employed for small articles such as bushes and the like. Owing to the high rate of production of this type of plastic it is not economical or necessary to use multiple tools for large articles.

Presses.

Hydraulic presses, crank presses and hand-screw presses are all used, crank presses being the most popular and best adapted for speedy output.

Two methods of moulding are recognised—hot moulding and cold moulding, but the distinction is not a sharp one owing to the many possible variations.

A Typical Method of Moulding.

The following method is typical of the

present practice in manufacturing moulded natural resin plastics.

20 lb. of shellac and 10 lb. of copal gum are fed into a masticator heated with 60 lb. per sq. in. of wet steam. When these binders are melted, which occurs in three or four minutes, 3 lb. of cotton flock are added gradually, followed by 50 lb. of slate dust and 3 lb. of carbon black. At the end of 15 minutes mixing is nearly complete and 15 lb. of scrap material is added. When the whole is

homogeneous it is extracted and passed through rolls to make it into sheets convenient to handle. (Fig. 2.)

Softening.

The sheets are taken to the press-shop and laid on hot-plates, situated beside the presses, to soften. The presses are of the crank-type driven by a belt from a line shaft. The bottom part of the mould is clamped to the fixed bottom plate of the press. The top tool is fastened by means of a set screw to the vertically acting ram. The mould is of the flash type and is kept at a constant temperature by means of gas jets, the top tool usually being a little cooler than the bottom.

Increasing the Plasticity.

When the material on the hot plate is soft, the operator takes a heavy hammer and "knocks it up," i.e., rolls it over and over with his left hand while hammering it with his right. This mechanical treatment brings all the material to the same temperature, and the pressure of the ham-

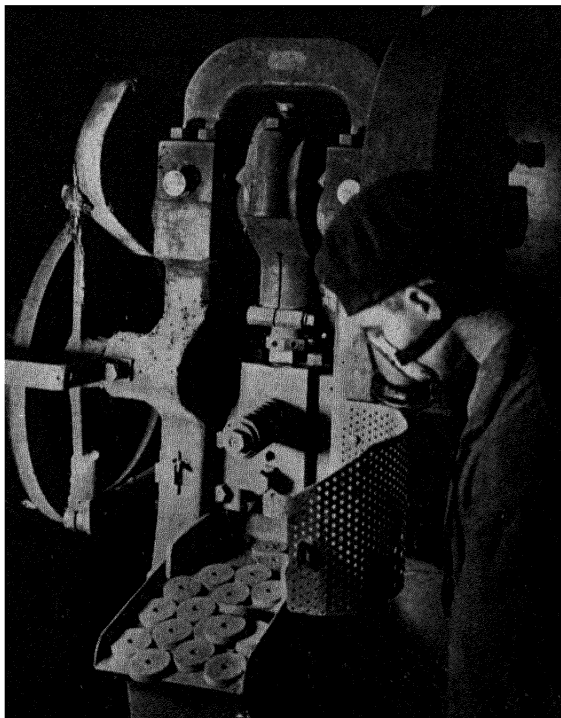


Fig. 3.—A BRIQUETTING PRESS.
Powdered moulding material is fed in the cold into a die which rapidly and automatically stamps it into a simple shape of known weight.

mer depresses the melting point of the binder, which suffers a time lag before recovering its correct value. In other words the plasticity is increased.

Utilising a crank press such as that shown in Fig. 4, the following sequence is carried out.

The floating metal inserts which it is desired to incorporate in the moulded article are anchored in position by means of the bolts shown in the front part of the lower tool.

Gauging the Temperature.

The tool itself is kept at the correct temperature (generally about 160° F.) by means of the gas-jet shown on the right-hand side of the press. A further jet is usually situated at the back of the press and underneath the tool. The operator judges the correct temperature by feeling the surface of the tool with the back of his hand. This method, with a skilled operator is just as reliable as taking the temperature by means of a surface pyrometer.

Inserting the Plastic Material.

A ball of the plastic material sufficiently large to form the article and to give a certain amount of spew is roughly pushed on the bottom tool and the short horizontal lever, shown on the left-hand side of the press communicating with the vertical connecting rod, is depressed. This throws in the clutch of the press and the top tool descends, guided not only by the dove-tailed slide, but, in addition, by the two dowel pins shown on the bottom tool

which engage with two corresponding holes in the top tool. Simultaneously with the closing of the press, an arm, seen just behind the operator's right shoulder, sweeps across the front portion, knocking careless hands away from the danger zone.

When the two halves of the mould have come together the excess of material squeezed out is removed and put back on the hot plate. A few seconds are allowed to elapse in order that the material inside

the mould may flow properly and take on its correct shape. Since the material is generally at a very much higher temperature than the tool, the former "sets" quickly on the surface and may be safely removed.

Removing the Article.

Removal is performed by depressing once more the lever on the left which throws again in the clutch and raises the top tool. The anchors are then loosened

by means of the brace shown on the right, and the article is ejected by lifting the horizontal piece of metal seen projecting from under the front of the press. This raises the lower interior portion of the bottom tool and the article is lifted out and placed on a tray.

Further metal inserts are then placed in the lower tool and secured by screwing up the anchors with the brace and the sequence of operations is repeated.

Fireproof Articles.

There exists a second class of composition, made from natural gums and oil,

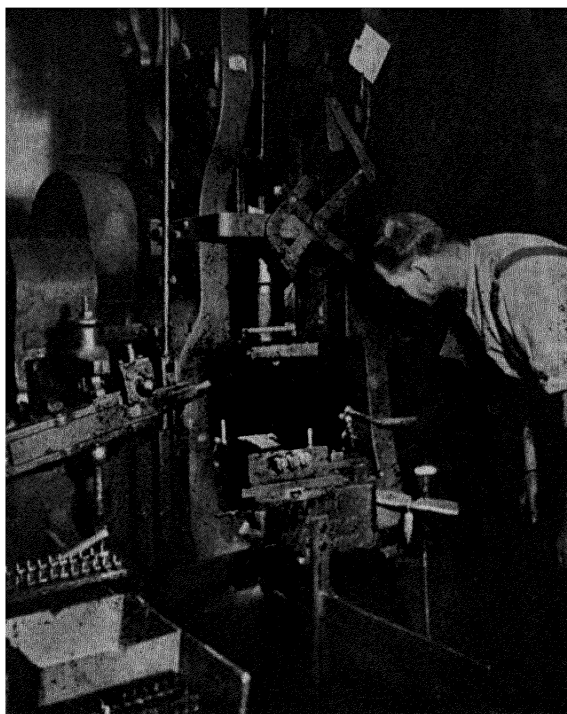


Fig. 4—A CRANK MOULDING PRESS.

used to produce the so-called fireproof articles; besides a third-class made from sodium or calcium silicate as binding agent and used chiefly for arc-shields.

The second class just mentioned is made from the same raw materials as the plastics just described but the method of treatment is a little different.

Binders and Fillers.

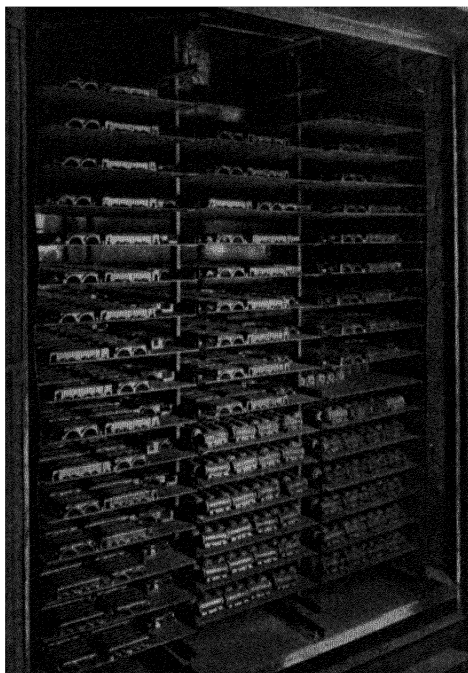
The binder usually consists of a natural gum made into a varnish with a drying oil thinned out with a volatile solvent. The maximum amount of fillers, usually short fibre white asbestos, is incorporated in a warm masticator where the major part of the solvent is driven off. The amount of binder present is usually insufficient to permit the material being rolled into sheets so it is ejected from the mixer in a coarsely powdered condition. Materials of this nature are generally pressed in the cold in a hydraulic press with a special valve. The crumbly and slightly cohesive mass is placed on the tool and the press is slowly closed. The special valve then comes into action and alternatively applies a high pressure and releases it several times. These pressure waves apply a hammering or tamping action which drives out all the air entrapped in the mass. The article is ejected by a subsidiary hydraulic ram in the base of the press.

Occasionally very dry materials are pre-formed in a briquetting press (Fig. 3), before moulding.

The Curing Ovens.

After seasoning in a current of air for a time the articles are then taken to the curing ovens where they are heated for a period and to a temperature which varies according to the shape and size of the article and the nature of the binding agent. The articles are placed carefully on trays which must be very rigid, for if the trays bend, the articles placed on them will be deformed. Generally perforated trays are used in order to permit of even heating.

The best type of oven is either a high-pressure water-heated oven or one which, if gas-heated, does not allow the products of combustion to come into direct contact with the articles being cured (Fig. 5). This is achieved by making the oven triple lined so that the hot gases circulate round the outside of the inner chamber. The two outer linings are designed to promote efficient thermal insulation to inhibit temperature fluctuations. As already indicated



Ebonestos Insulators, Ltd.
Fig. 5.—A TRIPLE LINED CURING OVEN.
The articles from the press are laid on trays which are perforated to allow even heating.

the time and temperature of heating can vary over very wide limits.

As an instance, the articles shown in Fig. 5 are heated for a period of 15 days, commencing at 120° F. and rising gradually to 600° F. The final polymerisation of the oils is then complete and the articles will not soften at any temperature and will resist the flame of a bunsen burner for three minutes.

Blistering and Warping.

The chief difficulties which are likely to arise during curing are blistering and

warping. Both may be caused by a too rapid rise in temperature. Blistering is also promoted if the period during which air - seasoning is carried out is cut down. Warping may be overcome in a variety of ways. For example portions containing threads, if the male and the female portion happen to be incorporated into different articles, may be made much more rigid and therefore less susceptible of blistering if the two portions are carefully screwed together prior to curing.

Similarly the stresses set up during cooling from 600° F. to room temperature may be minimised to some extent by case-hardening the articles by throwing them into cold water as they are extracted from the oven.

The Finishing Department.

Finally the articles are taken to the finishing department where all the rough burrs left from the pressing operation are trimmed off and the article is polished up on a buff and sometimes given a coat of lacquer by means of a spray pistol.

TESTING MOULDED ARTICLES.

Tests on moulded articles may be divided into :—

- A.—Physical tests ;
- B.—Electrical tests ;
- C.—Chemical tests ;
- D.—Machining characteristics.

A complete examination would involve the following, done at room

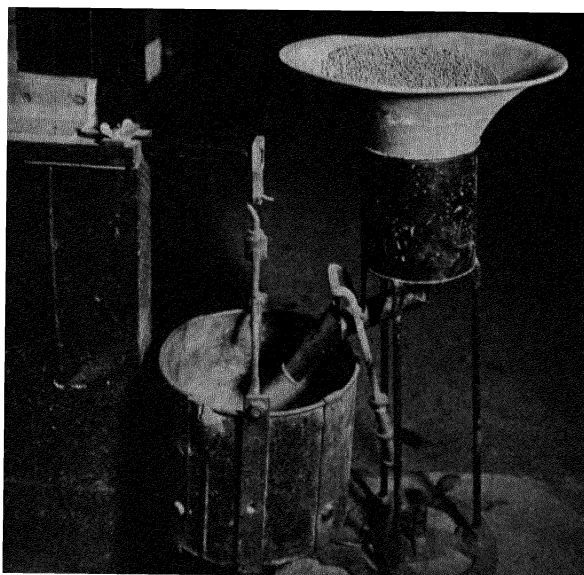


Fig 6 —TESTING CROSS BREAK STRENGTH OF MOULDED MATERIALS.

Lead shot runs into the container until the bar under test breaks, when the trip works and cuts off the supply of shot.

temperature as well as at higher temperatures, and after immersion in various media, especially transformer oil.

A.—Physical tests :—

- (1) Cross-break strength,
- (2) Impact value ;
- (3) Crushing strength ;
- (4) Tensile strength (though composite materials should never be used in tension) ;
- (5) Temperature resistance.

B.—Electrical tests :—

(1) Power factor.—This is easily the most important single electrical test. If this be good, most of the other electrical properties are likely to be reasonably good ;

(2) Breakdown voltage under carefully specified conditions ;

(3) Specific resistance ;

(4) Surface resistivity ;

(5) Resistance to arcing.

C.—Chemical tests :—

(1) Resistance to water ;

(2) Resistance to hot and cold oil ;

(3) Resistance to acids ;

(4) Resistance to alkalis ;

(5) Resistance to various solvents, e.g., alcohol and the like.

D.—Machining characteristics.

The precise tests to which any material is put naturally depends upon the use to which it is to be put.

For the rough evaluation of a new material or for works' control purposes the following simple tests are often applied :—

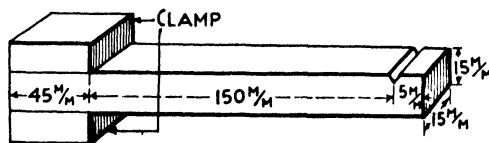


Fig 7. —TEST BAR FOR CROSS BREAK STRENGTH.

Cross - break Strength.

A moulded bar such as that shown

in Fig. 7 is used. It is supported at one end and a bucket is hung from the knife edge which sits in a notch at the other end. (Fig. 6.)

Lead shot is filled into the container, and drops through the orifice into the bucket. When the elastic limit of the bar is reached it breaks and the bucket falls, actuating as it does so a trip which cuts off the supply of lead shot. The bucket and contents are then weighed. The average of ten tests is taken and the cross-break strength in lbs. per square inch is calculated from the following formula:—

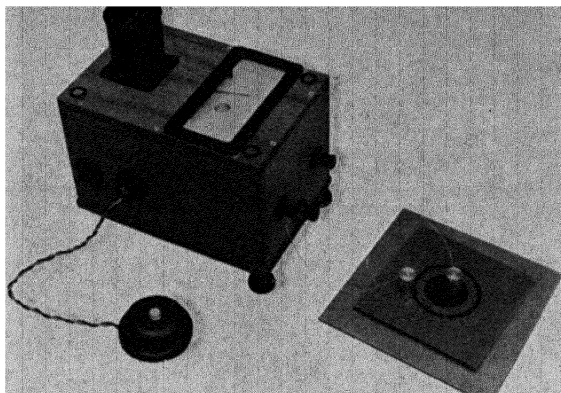
$$S = \frac{6WL}{BD^2}$$

Where S is the cross-break strength in lbs. per sq. inch; W, the weight of the bucket and contents; L, the length of the fulcrum and B and D the breadth and depth of the bar respectively.

Temperature Resistance.

The temperature resistance is graded according to the B.S.I. method by means of the deflection of a loaded bar situated in a constant temperature oven. A simple and rapid means of arriving at the grade temperature which, however, is not so accurate, consists in placing the material in water and gradually raising the temperature till it is just below the expected softening temperature. It is then extracted and a 7-lb. weight resting on a $\frac{1}{4}$ -in. diameter point is rested on the sample. The softening point is taken as that temperature at which the weight just fails to make an impression on the material.

For temperatures



Evershed and Vignoles.

Fig. 8.—THE SPECIFIC RESISTANCE MAY BE ROUGHLY TESTED ON A MEGGER.

above 100° C. an air oven may be used. It should be noted that because of the cooling effect of the water as it evaporates from the surface in the first case, the softening point is always found to be higher when tested by immersion in water than by immersion in an air oven.

Breakdown Voltage.

This is usually tested on a piece of the shape shown in Fig. 9. A 25 mm. disc is pressed into the hollow, good contact being obtained by means of a tin mercury amalgam or shredded lead. The other electrode consists of a flat disc 40 mm. diam.

A potential difference having a sinusoidal form and about 50 ~ is applied slowly so that breakdown occurs in about 20 secs. The test may be carried out under oil if flash occurs in air.

The result is expressed in volts per millimetre (R. M. S. value) from the following formula:—

$$B = \frac{V}{Tj}$$

where B = breakdown volts per millimetre; V, the voltage required to puncture the specimen; T, the minimum thickness of the specimen and j a junction varying with the thickness. For 1 mm. the value of j is 1.03; for 2 mm., 1.05; for 3 mm., 1.08; for 4 mm., 1.11, and for 5 mm., 1.14.

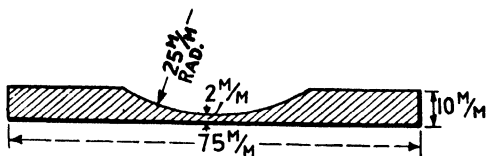


Fig. 9.—SECTION OF DISC USED TO DETERMINE BREAKDOWN VOLTAGE.

The puncture thickness may be decreased to 1 mm. (for 80,000 volts), or increased to 5 mm.

The Specific Resistance.

This may be roughly tested on a Megger such as that shown in Fig. 8.

THE CHEMISTRY OF CHROMIUM PLATING

By S. WERNICK, Ph.D., M.Sc.

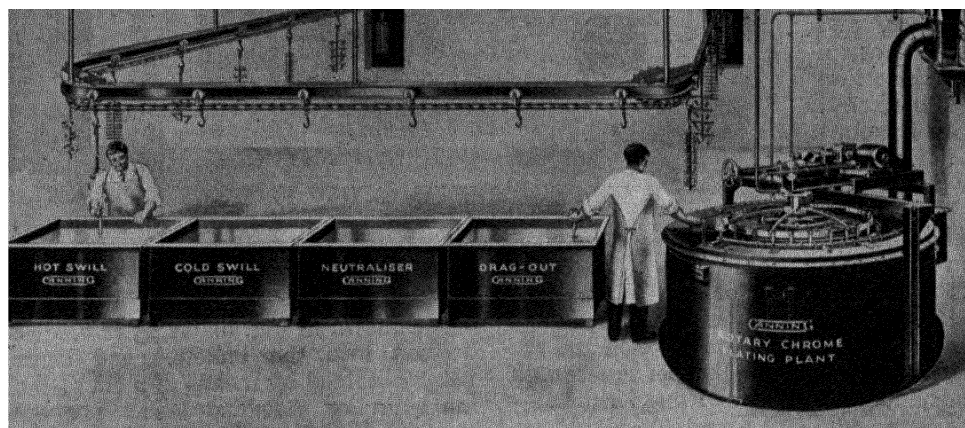


Fig. 1.—LAYOUT OF AN AUTOMATIC ROTARY CHROMIUM-PLATING PLANT.
Note the type of racks to which the articles are attached.

THE plant required in chromium plating differs considerably from the usual plant which is used in the deposition of the more common metals. The chromic acid electrolyte is highly reactive and must be contained in a tank which will reasonably resist chemical attack. While glass or stoneware are undoubtedly the ideal materials to use owing to their inertness, and may in fact be employed on a small scale, for the larger size units, vitreous or ceramic materials are too expensive and also necessarily fragile. Steel tanks are therefore used, since though iron suffers some attack, this has not been found to be serious. All joints in the tank are welded, and usually the walls of the tank are lined with wired-glass. The latter do not necessarily reach to the bottom of the tank, their purpose being to expose as little as possible of the steel surface to the solution and also to prevent the occurrence of short-circuiting.

Current Density.

A notable characteristic of chromium

plating is the relatively heavy current which requires to be applied in order to cause the metal to deposit. Thus, whereas, current densities of the order of 20 to 50 amps/ft.² are quite high in the deposition of other metals, e.g., nickel, copper, zinc, etc., while the current density used commercially in plating silver is not much higher than 4 amps/ft.², current densities exceeding 100 amps/ft.² are quite common with chromium.

Electrical Connections.

The high currents which are used require exceptionally heavy leads and bus-bar equipment to prevent over-heating at any point in the system, and all the electrical connections too, must be of a substantial character to conserve power. Good contacts must be made as between the anode bus-bar, the anode hooks and the anodes themselves, the hooks being in fact riveted to the anodes, while similarly, loose contacts must be avoided between the articles to be plated, the racks to which they are attached and the cathode bus-bar.

Anodes.

A further characteristic of chromium-plating plant is the use of an anode material which is other than the metal to be deposited: here again, it differs from the practice of plating the majority of other metals. Although chromium can be obtained in a pure state, it is produced in jagged, crystalline lumps, and it is difficult to produce it in the "slab" form in which other metals are usually cast or rolled. However, even if it could be obtained in this convenient form, it is highly expensive and if used as an anode, dissolves very efficiently. Since chromium deposits very *inefficiently*, one can readily appreciate that a system in which roughly eight times as much chromium dissolved in the electrolyte as become deposited at the cathode would be entirely unstable.

Apart from this, the chromium at the anode forms chromic acid, which is already the main constituent of the solution, and since chromium in this form is cheaper than the metal, it is obviously much cheaper to replenish the metal in the electrolyte by adding chromic acid as it is required, while making use of an anode which is inert and does not affect the composition of the solution. This has in fact been done, the anode material which is widely in use being a suitable form of lead. A chemically pure lead which is first made the anode in a sulphuric acid bath, forming a film of lead peroxide on the surface, has been found to be satisfactory. This film protects the anode and prevents formation of the lead chromate.

Another successful lead anode contains a proportion of antimony in its composition, this alloy being also used in the accumulator industry. The lead chromate which forms on the surface of the antimony-lead alloy is found to be loose, owing to the formation simultaneously of antimony oxide and can, therefore, be readily removed by burnishing.

One of the most recent lead anodes which has been developed contains a small proportion (about 0.2 per cent.) of tellurium; apart from its excellent physical properties, it is highly resistant to chemical corrosion.

Solution Control.

The chemical control of the chromium-plating electrolyte is highly important, since it is particularly sensitive to changes

in the relative concentrations of its constituents, which in time materially affect the performance of the bath.

Additions of all kinds of chemicals have from time to time been recommended to the chromic acid which is the main constituent of the solution, but the only other essential constituent is the sulphate radicle in some form—preferably as sulphuric acid, though it may be added as chromium sulphate. It is added in relatively small amount and its concentration is critical.

Typical Chromium Plating Baths.

Thus, two typical types of chromium-plating bath contain respectively:—

	Bath No. 1	Bath No. 2
	gms./litre.	gms./litre.
Chromic acid ..	250	400
Sulphuric acid ..	2.6	4

It will be noticed that the ratio of chromic acid to sulphuric acid is approximately equal to 100, and this, roughly, is the proportion in which it is desirable to hold them. While a change in concentration of a few grams in the chromic acid content affects the relationship but slightly, a similar change in the sulphate content materially alters the ratio and since this might have serious consequences in the production of chromium-plating of good quality, it is necessary particularly to exercise close control of the concentration of sulphate.

Chemical Changes in the Electrolyte.

It is now known that quite profound changes occur in the chromium-plating solution, despite the fact that only two constituents are present at the commencement. Essentially, the chromic acid which contains the chromium atom in a high state of oxidation is reduced at the cathode to form a chromic salt which combines with sulphuric acid to form chromium sulphate, while some also combines with chromic acid radicles to form chromium di-chromate. The presence of these compounds, from which the metallic chromium eventually deposits, gradually changes the colour of the solution from a clear translucent reddish tint to an opaque brownish-red. Excessive quantities of these reduction compounds are highly undesirable, and, unfortunately apart from their occurrence in the solution through the natural action of electrolysis, they are readily augmented

by contact with iron (when ferric dichromate is formed). Contact with iron arises through the tank material, or articles which are plated which may be of iron.

The chromate or di-chromate part of the radicle in any excess of these substances which may arise is abstracted from the chromic acid proper in the electrolyte and is virtually therefore "locked up" and in this condition represents wasted material which "clogs" the solution when present in any quantity. It has the added disadvantage of rendering it difficult to obtain an idea of the concentration of the "active" chromic acid present by any other method than chemical analysis. Thus, although one could arrive at a sufficiently accurate figure of chromic acid concentration by a simple specific gravity test, with a new chromic acid solution, such a figure would be wholly misleading if taken in the presence of large concentrations of chromates and di-chromates.

Determination of Composition.

Since specific gravity determinations may thus err considerably from the true value, and in any case give no clue to the sulphate content, methods of the following type are commonly employed to determine the correct composition.

Estimation of Chromic Acid (due to Haring and Barrows).

The following solutions are employed :—

(1) *Dichromate solution*.—Dissolve 5.884 gm. of pure potassium dichromate in 1 litre of water ;

(2) *Ferrous ammonium sulphate solution*.—Dissolve about 40 gm. of this salt and 75 c.c. concentrated sulphuric acid in 1 litre of water ;

(3) *Potassium permanganate solution*.—Dissolve about 3.2 gm. of this compound in 1 litre of water.

The procedure is as follows :—

It is first necessary to determine the ferrous sulphate equivalent of the permanganate solution, thus : 25 c.c. of the ferrous sulphate solution are diluted to about 300 c.c. in a beaker and 25 c.c. of concentrated sulphuric acid are added. This solution is now titrated against the permanganate solution until a persistent pink colour is produced.

The ferrous sulphate solution is now standardised against the standard di-

chromate solution as follows : A 25 c.c. sample of the latter which is equivalent to 1/10th gm. CrO_3 , is diluted to about 300 c.c. and 25 c.c. of concentrated sulphuric acid is added. After cooling to room temperature, 50 c.c. of ferrous sulphate which is more than sufficient to reduce the chromic acid is added, and the excess is titrated with the permanganate, until the "end point," which is somewhat masked by the colour of the solution but, nevertheless, readily detected if looked for, is reached.

A correction for the volume of permanganate required to produce the "end point" can be made by boiling the solution for ten minutes (which destroys the excess of permanganate), cooling to room temperature, and again titrating to the same point. The small volume of permanganate required the second time is termed the "colour correction," which, when subtracted from the volume used the first time, gives the true permanganate equivalent of the excess ferrous sulphate. The ferrous sulphate actually required for the reduction of chromic acid, and hence the equivalent of the ferrous sulphate in terms of chromic acid can then be readily calculated.

Determination of Sulphate Content.

This is best carried out gravimetrically by precipitating the sulphate with barium chloride, the barium sulphate formed being weighed. Since barium chloride shows a tendency to form barium chromate in chromic acid solutions, the usual operation is modified by the addition of alcohol which reduces the chromic acid to chromic chloride on heating.

The estimation is carried out as follows :

10 c.c. of the electrolyte is placed in a clean beaker to which 100 c.c. of distilled water, 10 c.c. of pure concentrated hydrochloric acid and 10 c.c. of alcohol are added. The mixture is boiled until the volume of the solution has been reduced to less than 25 c.c. after which 100 c.c. of distilled water is added and the solution brought to boiling point. About 10 c.c. of a 5 per cent. solution of barium chloride is then carefully added drop by drop and the solution is then left to stand overnight so that the precipitation may be complete. The solution is then at first decanted and finally filtered through a suitable grade of filter paper. It is

transferred to a weighed crucible and carefully ignited by heating the crucible strongly. When all the filter paper has been burned away, the crucible is transferred to a desiccator, allowed to cool and then reweighed. If it is desired to express the result in terms of concentration of sulphuric acid this may readily be obtained by multiplying the weight of barium sulphate found by the factor, which is 0.42.

Operating Conditions.

The conditions of operating a chromium-plating solution have already been briefly touched upon. The current density which is employed is abnormally high for plating work and it varies appreciably with the composition of the solution and the temperature which is maintained. The usual operating conditions for a bath containing about 25 per cent. of chromic acid are a working temperature of 30–40° C., and a current density of 100 to 150 amps per square foot. With a solution which is richer in metal content and which is, therefore, less resistant to the passage of current, lower current densities are employable and at a correspondingly lower voltage.

Types of Deposit Produced.

The type of deposit which is commonly met, i.e., the brilliant blue-grey finish, is not the only kind of plating obtainable from the chromium-plating bath. Indeed, this has been found to vary quite definitely with the conditions of deposition, and three distinct kinds of deposit have been distinguished. As the current density rises, the following types of deposit are successively produced:—

- (1) A matt deposit possessing a certain degree of brightness, which is best described as "milky";
- (2) A brilliant deposit;
- (3) A matt deposit which is definitely dull.

It is the second type of deposit, which is hard and requires no subsequent polishing, that the plater aims at producing. The first deposit is too thin and unattractive to have any commercial value, while the third, though thick, would require considerable final polishing before it attained to the brightness of the intermediate deposit.

These three typical deposits are also obtainable, *but in the reverse order*, on

increasing the temperature of the solution at a given current density, and these facts indicate the importance of selecting the correct range of temperature and current density in chromium-plating practice.

Practical Aspects of Chromium Plating.

The low cathode efficiency and low-throwing power of chromium plating baths make it necessary to employ special methods of disposing the "work" to be plated in the bath. The articles are commonly firmly attached to a rack the shape of which is specially devised according to the size and shape of the articles to be plated. The articles on the rack are so disposed towards the anodes that they allow the current to pass as uniformly as possible over the surface. In the case of deeply recessed articles, e.g., the inside of a deep bowl over the whole surface of which it is required to chromium plate, it may be necessary to use what is termed an "auxiliary anode." The latter consists of a suitably shaped piece of lead which is attached to the anode bus-bar and is sufficiently portable in the solution to allow it to be moved in any position relative to the articles attached to the cathode.

While recessed parts of a cathode may receive little or no deposit, conversely those parts which are nearer to the anode may receive excessive metal, which then no longer appears bright but unattractively dull, the deposit being then said to be "burnt" locally. This is particularly the case with articles which project sharply. To overcome the difficulty, it may be necessary to "shade" such parts by looping wire round them, which then takes up the excessive current. The same difficulty may result in an article which is attached to the cathode by means of a wire through a hole receiving no plating below or in the immediate neighbourhood of such holes, etc. In this case, it may be necessary to block the hole up with some suitable material which is relatively inert to chromic acid, e.g., cork, when the gassing is reduced and the plating is found to deposit satisfactorily.

It is apparent, from the foregoing, that very considerable skill must be shown by the operator in the racking and the general disposal of articles of diverse shape for chromium plating; and the success which

attends his efforts is as much dependent on carefully planned methods of tackling each different type of article as to meticulous control of the solution and the operating conditions employed.

Dangers to Health.

For the benefit of those who have had little or no experience in the operation of a chromium plating plant, and who may contemplate doing so, it is necessary to emphasise the fact that there is considerable health hazard to the plater unless correct precautions have been taken to dispose of any possibility of contact with chromic acid spray, or even the chromic acid electrolyte. Inhalation of the spray is dangerous since it seriously affects the delicate membrane in the nose and throat, and may also give rise to dermatitis of the skin. Sores which occasionally form on the hands and arms through contact with the chromic acid may be extremely painful and are usually difficult to heal rapidly.

The possibility of undesirable effects of this type may, however, be reduced to negligible proportions by the use of efficient exhaust plant, which is attached to the sides of the plating tank and usually connected to a condensation chamber into which a powerful fan sucks the spray and condenses the electrolyte which it contains. Expert advice should be sought by those contemplating the installation of a chromium plating plant, since the efficiency of the exhaust system is required to comply with Home Office regulations, which also provide for the regular inspection of the plating premises and the workers employed as operators. If the regulations are complied with, little trouble may be feared under this head.

USES OF CHROMIUM PLATING.

Wear Resistance.

Chromium plating is most commonly known as a stainless and decorative finish, and it is, therefore, not so widely appreciated that it possesses additional unique properties which make it useful in other fields, in which it has accordingly been applied.

Thus, chromium is a very hard metal and the deposit has been found to be even harder than that obtained by the usual methods of production. Its hardness does in fact vary with the conditions of deposition, but in general, chromium deposits, as a result of their hardness, have been found to wear remarkably well. It has accordingly been used on engineering parts which are subjected to continued abrasion, on gauges which are required to retain their dimensions, and on moulds used in the production of Bakelite articles which are subjected to high pressure, the mouldings being then produced with a higher surface lustre. Again, printing plates which are required to withstand heavy wear, are chromium plated to-day. Thus, engraved plates which are used for printing bank-notes which are produced in very large quantities, have been found to give very prolonged service as a result of the chromium coating which is applied.

Resistance to Chemicals.

The resistance of chromium to chemicals, due to its comparative inertness, is fully realised in the plate. Thus, it is little affected by the common mineral and organic acids, with the exception of hydrochloric acid, which is a convenient means of stripping faulty deposits upon nickel, the latter being relatively unaffected, particularly in the short contact which it is likely to have with the acid in the stripping process. A special field for chromium plating is upon goods, e.g., tools, which come into contact with sulphur compounds to which the metal is highly resistant. Corrosion due to sulphuretted hydrogen, which occurs on metal parts in contact with illuminating gas for example, can be largely prevented by the application of the chromium deposit. Apparatus used in oil-cracking and the vulcanising of rubber may, similarly, be protected from the effects of sulphur compounds. In point of fact, corrosion by sulphur, sulphides and sulphur compounds generally, which has in the past always presented an important problem to many industries has been overcome in a number of cases by the use of the chromium deposit.

THE MANUFACTURE OF HYDROCHLORIC ACID

By M. D. CURWEN, B.Sc., A.I.C.



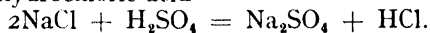
Fig. 1.—BATTERY OF CONTINUOUS HYDROCHLORIC ACID FURNACES.

Salt and sulphuric acid are fed in at the top. On the bottom floor note the water-cooled trommels, where the salt cake is removed.

THE earliest method of producing hydrochloric acid was by heating sea-salt with clay. This manufacture was carried out in the middle of the eighteenth century, and it is interesting to note that in recent years attempts have been made to produce the acid by similar methods, using calcium, magnesium potassium and sodium chlorides. Many patents have been taken out, but as far as is ascertainable such methods have been commercially unsuccessful, or at least negligible.

There was little use for hydrochloric acid in the eighteenth century and for many years after. In the early part of the nineteenth century when soda became so important to the life of our great textile industry, Leblanc was producing sodium sulphate or salt cake in order to produce sodium carbonate therefrom. The method

he employed was to heat common salt with sulphuric acid, giving salt cake and hydrochloric acid



The salt cake was the desired product while the hydrochloric acid was a product—and a noxious one. It was undesired and allowed to escape into the atmosphere, with the result that a great amount of damage to localities in the middle of the nineteenth century were passed compelling to condense the acid vapour

Importance of Hydrochloric Acid

With the passage of time, sodium sulphate as a soda manufacturer's ammonia-soda. However, as the

increased, the above method of manufacture by no means disappeared. To-day enormous quantities of hydrochloric acid are used: in the steel and other metal industries for "pickling" or cleaning, in the extraction of phosphates from bones, in scouring textiles, in hydrolysis, in dye-stuffs manufacture, in general neutralising alkaline liquors and in the making of a great number of metallic salts for use in a diversity of industries.

Furthermore, the sodium sulphate which has now become the by-product is purified to make the well-known Glauber salts.

Various Modern Methods.

By far the greatest quantity of hydrochloric acid made is still produced from salt and sulphuric acid, some by the old batch method and some by the newer continuous processes. During the war when large quantities of nitric acid were being made, the residue nitre cake, which consists of sodium hydrogen sulphate with some free sulphuric acid, was used to replace sulphuric acid.

The most modern method, but by no means universal, is that of manufacturing the acid from its constituent elements, hydrogen and chlorine. This process is utilised where it is economically feasible, that is, where hydrogen and chlorine are cheap. For example, the process of producing caustic soda by electrolysis of brine, also produces hydrogen and chlorine.

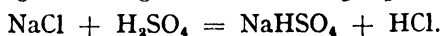
Use of these two gases is limited, hydrogen for welding and chlorine in making chloride of lime, general ion and chemical processes and massive production has resulted in it being feasible to install a plant for the production of hydrochloric

It should be remembered that chlorine is produced during the electrolysis of brine, so that the acid is made in the same plant during the production of synthetic

Production from Common Salt.

The Batch Process.—This process, similar in method to that carried out in the early nineteenth century, is still pursued. In essence the plant consisted of a cast-iron pan set in a furnace in juxtaposition to a reverberatory hearth.

Charges of salt and of acid (S.G. 1.7) are added to the pan, the quantity of the cheaper raw material salt, being in excess of the theoretical. The reaction takes place at a low heat with evolution of hydrochloric acid gas. At this temperature total conversion to sodium sulphate does not take place, the reaction proceeding according to the following equation:



The mass is then raked to the reverberatory hearth where under greater heat the sodium acid sulphate reacts with unacted-upon salt:

$$\text{NaCl} + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HCl}.$$

It will be obvious from the drawing that the heating gases pass over the surface of the mixture, and the acid produced is consequently impure

and dilute. Another type of furnace in which heat is applied throughout externally produces a purer acid.

The gases are conducted to an absorption system which will be described later.

The Continuous Process.—Various methods of producing hydrochloric acid and sodium sulphate continuously from one machine have been devised. One modern type consists of a rotary kiln in which salt and acid (or nitre cake) are mixed and then pass to a hot zone in the kiln where the main reaction takes place. Heat is supplied in the form of burning gases which pass in the opposite direction to the feed.

Another modern type of continuous furnace is that seen in Fig. 1. The essential features are a shallow pan and a central shaft carrying stirrers or rabblers, with automatic feeds for acid and salt and an automatic device for removing the residual salt cake.

Common salt is brought to the loading floor on top of the furnace by rubber-belt conveyers to salt hoppers. These are

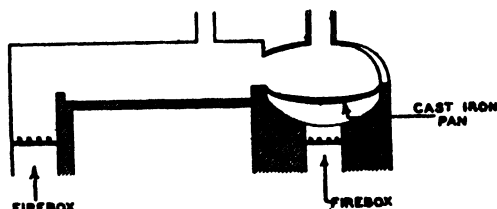


Fig. 2.—OPEN ROASTER.

fitted with worm feeds passing the salt into a cast-iron tube and so to the bed of the furnace continuously.

Automatic measuring vessels supply 93 per cent. sulphuric acid into an acid pot inside the furnace where it is distributed over the surface of the salt. Each of the furnaces shown in the photograph is capable of producing 100 tons of hydrochloric acid and 56 tons of salt cake per week. As the reaction within the furnace proceeds the residual salt cake is driven

from the centre of the pan to the periphery by means of four arms fitted on the central driving shaft, until it is automatically discharged through a water-cooled trommel. The gases escape through the top of the furnace and are removed by means of a fan to the absorption system.

Synthetic Hydrochloric Acid.—As was already pointed out, this process is more or less confined to factories which produce hydrogen and chlorine gases as by-products during the manufacture of caustic soda by the electrolysis of brine.

It has long been known that when hydrogen is burned in an atmosphere of chlorine, hydrochloric acid is formed and the synthetic process has been made possible commercially only as a direct result of electrolytic caustic soda. The modern plant for this manufacture is essentially very simple, consisting of a cylindrical combustion chamber carrying two burners, one in the middle for hydrogen and the other surrounding it for chlorine. The hydrogen is first ignited and then the chlorine is admitted, both supplies being regulated by suitable means. In some works, the feeds are controlled

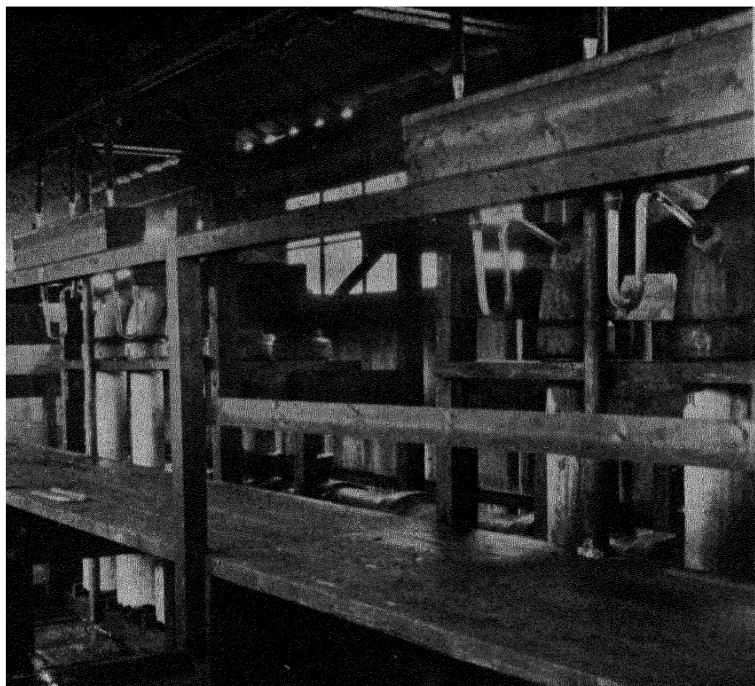


Fig. 3.—TOP OF VITREOSIL ABSORPTION SYSTEM.
Showing feed of water or dilute acid.

electrically, a failure in the current causing a magnet to drop and shut off the supply of hydrogen so that the possibility of explosion is avoided.

The cylindrical combustion chamber is made of Vitreosil (fused quartz), the most suitable material for conveying hydrochloric acid vapours and at the same time for withstanding sudden changes of temperature.

Absorption of Hydrochloric Acid Gas.

Hydrochloric acid is almost invariably utilised as a solution in water and the bulk is produced as a 31-32 per cent. solution. Many systems have been evolved to absorb hydrochloric acid gas, but, since they differ generally merely in detail, we shall refer mainly to one type.

In the early days when the acid was a by-product and the laws compelled manufacturers to condense the gas, the exit vapours from the Leblanc process were drawn through a coke-packed tower down which trickled water for the absorption. The method was fairly effective, but from modern chemical engineering standpoints crude, since little was known

as to the requirements of a proper condensing system. Today it is realised that absorption depends upon the temperature of the entering gases, the concentration of hydrogen chloride and the time of contact between the gas and water (or dilute acid), and modern plants have been designed with a full knowledge of these facts.

Material of Construction.

Since hydrochloric acid is extremely corrosive, the material in which the plant is constructed is of great importance. Where the gases issuing from the furnace are relatively low in temperature—for example, in manufacture by the open roaster or synthetically—then all pipes and tubes leading immediately from the plant and throughout the condensing system must be of earthenware or Vitreosil. The cementing material is generally tar and asbestos.

Where the issuing gases are hot, in other words no condensation is possible, they may be conveyed to the condensation system through iron pipes since "dry" hydrogen chloride has little action on the metal. As soon as the gases reach condensation temperature, the above again applies.

The Tyler Absorption System.

Although there are many systems it is convenient to describe this one in which the entire absorption is carried out in

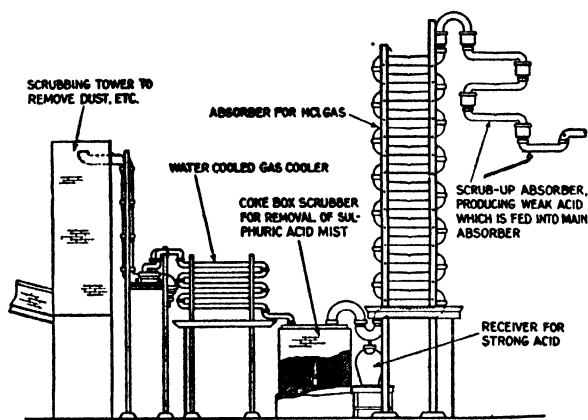


Fig 4—TYLER SYSTEM OF ABSORBING HYDROCHLORIC ACID GAS.

mist and now arrive at the base of the absorption tower. This, as will be seen from the accompanying drawing, consists of a series of S bends of flattened silica tubing in which small ridges maintain a quantity of the absorbing medium. In the topmost bend is fed the water (dilute acid is also used), this trickling slowly down, becoming stronger and stronger until it is finally drawn off into a storage tank.

Fig. 4 shows a method of feeding the dilute acid into the topmost silica bend. Here the liquid is fed into rubber-lined distributing boxes by means of glass tubes. The concentrated acid which issues from the bottom has a strength of 28-36° Twaddell.

Impurities in the Acid.

Acid produced from salt and sulphuric acid contains many impurities present in the latter, namely, arsenic, selenium and lead in addition to sulphuric acid itself, chlorine and iron from the pot. A pure acid may be obtained, e.g., by the addition of barium sulphide to remove arsenic followed by a distillation of hydrochloric acid gas into pure water.

plant made of Vitreosil (fused silica).

The gas is first passed through a dust scrubber and then to a water cooler in order to obtain the maximum efficiency in absorption. The vapours then enter a coke scrubber (if the salt-sulphuric acid method has been used) to remove sulphuric acid

THE INDIA RUBBER INDUSTRY

PART III.—ANALYSIS AND TESTING OF RAW MATERIALS

By J. R. SCOTT, Ph.D., F.I.C.

Research Association of British Rubber Manufacturers

ON page 1264, the nature and functions of the various raw materials used in the rubber industry have been described. These materials are so numerous and varied that a whole book might be written on the many tests involved in their complete examination; only the most important of these can be dealt with in the present article.

The analytical and other tests applied to the raw materials of rubber manufacture may conveniently be divided into: (i) tests on the raw or crude rubber; (ii) tests on reclaimed rubber, or "reclaim"; (iii) tests applied generally to fillers, reinforcing agents, and other powdery ingredients; (iv) specific tests applied to individual ingredients or materials; (v) tests on fabrics used in conjunction with rubber.

TESTS ON RAW RUBBER.

The analytical test most commonly applied to raw rubber is that of "acetone extract."

Acetone Extract.

This extract is a measure of the amount of certain non-caoutchouc constituents of the rubber, usually termed collectively "resins." In normal plantation smoked sheet, or crêpe, and in Para (Brazilian) rubber the extract ranges from about 2

to 3.5 per cent. A markedly higher figure is usually a sign of an inferior rubber.

To determine the acetone extract, the rubber is cut into pieces about 1 to 2 mm. cube, or, if a roll mill is available, rolled out into a thin sheet. About 5 gm. of the rubber is then weighed out and spread, or laid, on a piece of filter paper, which is then rolled up with the rubber inside; this prevents the rubber agglomerating to a solid mass under the action of the hot acetone. The whole is now inserted in a paper extraction thimble and placed in an extraction apparatus, of the Soxhlet, Schidrowitz, or similar type (various forms are shown in Fig. 1). 50 c.c. of acetone is placed in the extraction flask or tube, which is then heated on a water-bath, so that the acetone boils gently. The vaporised acetone condenses on the condenser and drops into the extraction thimble, where it dissolves the "resin" from the rubber. In some

types of apparatus (b and c in Fig. 1) the acetone collects in the glass thimble until this is full and then all siphons over, whilst in others (a and d) the acetone drains straight through the thimble back into the extraction flask or tube.

Extraction is continued for seven hours without interruption. The

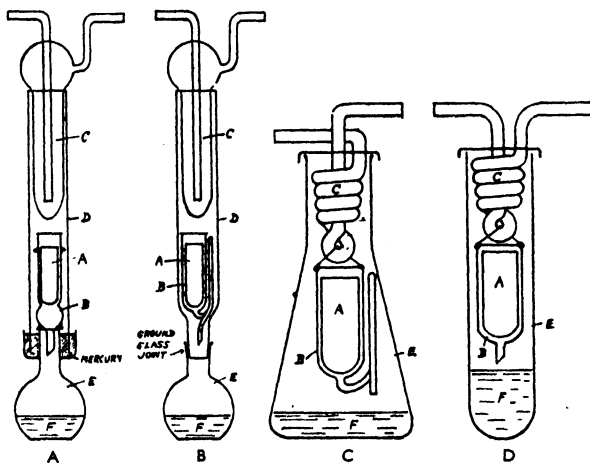


Fig. 1.—TYPICAL APPARATUS USED FOR EXTRACTING RUBBER, ETC., WITH ACETONE (OR CHLOROFORM).

A = paper extraction thimble; B = glass thimble; C = condenser; D = condenser jacket; E = extraction flask or tube; F = acetone (or chloroform).

extract is then poured into a CO₂ flask (previously dried at 65 to 70° C., cooled in air, and weighed), and the extractor rinsed out with 15 c.c. acetone. The acetone is then distilled off on the water-bath, and the flask containing the residue dried in a current of air for one hour at 65 to 70° C., cooled in air, and weighed. (Note.—If an apparatus of type *d* is used, the acetone can conveniently be distilled off and the residue dried in the extraction tube itself.) The weight of the residue, expressed as a percentage of the weight of rubber taken, represents the "acetone extract."

The acetone used must be freshly re-distilled, and the filter paper and paper thimble must be extracted with acetone before use.

TESTS ON RECLAIM.

Acetone Extract.

In the case of reclaim, this is essentially a measure of the amount of oils, or other softeners, that have been added in the course of manufacture.

It is determined in the same way as for raw rubber, except that a smaller amount (about 2 gm.) suffices, owing to the larger amount of extractable matter (about 6 to 10 per cent.) normally present.

Chloroform Extract.

It is generally considered that an excessive amount of chloroform-soluble matter, which is mainly depolymerised rubber, is a sign of an inferior reclaim, hence it is usual to determine the "chloroform extract."

After carrying out the acetone extraction, the flask, or tube, containing the acetone is immediately replaced by one containing 50 c.c. of chloroform, and extraction is continued with this for four hours, or longer if the liquid from the extraction thimble is still coloured. When extraction is complete the chloroform is distilled off and the residue dried in exactly the same way as the acetone extract (see above).

Ash.

As the mineral ingredients of a rubber mixing have a considerable influence on the properties of the product, it is important to know the amount and nature of the mineral substances present in

reclaim. The amount of such substances can be determined approximately by incineration, and their nature by an analysis of the ash according to ordinary analytical methods.

To determine the ash, about 2 gm. of the reclaim is weighed out into a tared porcelain crucible, which is then heated gently by a small bunsen flame. Care is necessary to prevent loss by spurting after the mass melts and to avoid the vapours taking fire. (It is convenient to rest the crucible in a hole in an asbestos sheet.) When all the volatile matter has been driven off and a charred mass remains, the temperature is raised to a dull red heat (about 500° C.), preferably in a muffle furnace where the temperature can be more accurately controlled. When all the carbon is burnt off, the crucible is cooled in a desiccator and weighed; the heating should be repeated until the weight is substantially constant.

Specific Gravity.

This must be determined in order to be able to calculate the specific gravity of rubber mixings in which the reclaim is used. Specific gravity is usually determined by the familiar method based on the principle of Archimedes, that is by weighing a sample in air and again suspended in water, the specific gravity being then calculated by the formula:—

$$\text{specific gravity} = \frac{\text{weight in air}}{(\text{weight in air}) - (\text{weight in water})} \times \text{density of water.}$$

For most practical purposes the density of water can be taken as 1.

GENERAL TESTS FOR COMPOUNDING INGREDIENTS.

Moisture.

As rubber mixings are usually vulcanised by heating above 100° C., the presence of moisture is liable to cause porosity, owing to the conversion of the moisture into steam. It is therefore important that all powders used in any considerable quantity should be substantially dry, a moisture content of two per cent. being regarded as the maximum allowable.

To determine moisture content, a wide shallow stoppered weighing bottle (say, three inches diameter by one inch deep) is dried at 110° C., cooled in a desiccator, and weighed. About 2 to 5 gm. of the

material under test (depending on its density) is weighed out into the bottle and spread evenly over the bottom. The bottle, with the stopper removed, is heated in an oven at 110°C . for two hours and then transferred, along with the stopper, to a desiccator to cool. It is finally removed from the desiccator, the stopper immediately inserted, and the whole weighed. The heating and weighing are repeated till the weight is constant.

The loss in weight is mainly due to moisture, and is normally taken as a measure of the moisture content.

Grit.

The presence of coarse gritty particles is undesirable, because they form points of weakness in articles subjected to severe stresses (e.g., tyres), spoil the appearance of thin sheet or fine moulded goods (e.g., bathing caps), and tend to collect in the machines used for "spreading" and "extruding," causing streaks on the finished article. All powders used in rubber mixings should, therefore, be tested for the presence of coarse grit.

A standardised apparatus and technique for this purpose have been evolved. The apparatus is the "Gallie-Porritt grit tester" illustrated in Fig. 2. It consists of: (i) a funnel, A, with threaded outlet tube, B; (ii) a flanged tube, C, attachable to B by the nut D; (iii) a sieve cup, E, having a circle of wire gauze, K, of the desired mesh soldered over the bottom; (iv) a jet, F, supplied with water from the mains through the filter, G; (v) an auxiliary jet, H. Sieves with 100, 200, and 300 meshes per linear inch are normally provided.

The mode of operation is as follows:—The sieve-cup is dried at 100°C ., weighed, and inserted as shown. A weighed quantity (preferably 100 gm.) of the powder is placed in the funnel and wetted with water from the auxiliary jet, H,

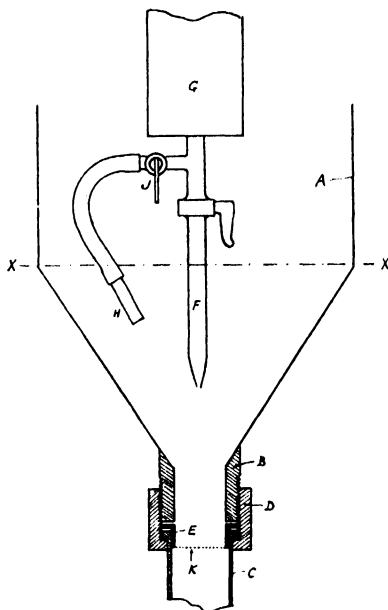


Fig. 2.—DIAGRAM SHOWING THE CONSTRUCTION OF THE "GALLIE-PORRITT GRIT TESTER."

until the funnel is about half full. If the powder is one that does not wet easily (e.g., sulphur) a little methylated spirit helps. The high-pressure jet, F, is now gradually turned on full, and its height above the sieve is adjusted so that the water level tends, if anything, to fall, the auxiliary jet being used to keep the level at about XX (see figure), and to wash down any solid from the sides of the funnel. The high-pressure jet keeps the contents of the funnel in vigorous circulation, and by impinging on the sieve, breaks up aggregates of powder and drives the fine material through the sieve.

When the water issuing from C is perfectly clear, the jet F is turned off and any material on the sides of the funnel is washed down on to the sieve by the jet H. Nut D is now unscrewed and the sieve-cup, containing the gritty residue, is removed, dried at 100°C ., and weighed to determine the weight of the grit.

Copper and Manganese.

The perishing or "ageing" of vulcanised rubber may be greatly accelerated by even the minutest traces of copper or manganese compounds. It is, therefore, essential that all materials used in rubber mixings should be substantially free from these impurities. The exact quantitative estimation of traces of copper and manganese naturally varies according to the nature of the material under test, so that full details of all these methods cannot be given in this brief article. For most practical purposes, however, the following qualitative, or rough quantitative, methods are sufficient to detect dangerous amounts of these impurities.

Copper.—1 gm. of the material is dissolved in 25 per cent. nitric acid, or, if insoluble, boiled with 15 c.c. of the acid. The solution is filtered if necessary, and an excess of ammonia added. Any

precipitate that forms is filtered off and the colour of the liquid examined. Any trace of a blue colour indicates the presence of copper in dangerous amounts.

If it is desired to estimate the copper quantitatively, this can be done with the ammoniacal solution, after boiling off the excess of ammonia.

Manganese.—A rapid qualitative test suitable for white powders consists in strongly heating the powder with caustic potash and a little potassium chlorate in an inverted porcelain crucible lid. If manganese is present, a green colour will develop in the fused mass, owing to the formation of potassium manganate.

For a quantitative test, 1 gm. of the powder, mixed with 5 to 6 gm. of a 50 : 50 mixture of potassium and sodium carbonates, is fused in a crucible for half an hour. The mass is cooled, dissolved in water and filtered, and the residue on the filter is washed with hot water and dissolved in 30 c.c. of 30 per cent. nitric acid.

TESTS FOR ANTIMONY SULPHIDE. Free Sulphur.

As the proportion of sulphur in a rubber mixing needs careful adjustment, it is essential to know how much free sulphur is present in an ingredient, such as commercial antimony sulphide, which may contain considerable amounts of it.

Converting to a Soluble Form.

As some of the sulphur may be present in an amorphous form insoluble in carbon disulphide, this must first be converted into a soluble form by heating the antimony sulphide at 150° C. for five hours in an ammoniacal atmosphere obtained by placing a wad of cotton wool wetted with strong ammonia solution in the oven.

Making the Test.

About 1 to 2 gm. of the antimony sulphide is then weighed out into a paper extraction thimble, which is plugged with fat-free cotton wool and extracted with carbon disulphide for eight hours in an apparatus similar to that used for acetone extraction (see Fig. 1). After evaporating off the carbon disulphide from the extract, the residue is dried for one hour at 65 to 70° C. The weight of the residue, ex-

pressed as percentage of the weight of antimony sulphide taken, represents "free sulphur."

Calcium Sulphate.

Commercial antimony sulphide usually contains more or less calcium sulphate, and as this reduces the pigmentary strength of the material, it is important to know the amount present.

1 gm. of the antimony sulphide is weighed out and mixed with 4 gm. of resublimed ammonium chloride in a weighed porcelain crucible. This is then heated to convert the antimony sulphide into antimony chloride, which is volatilised along with the excess ammonium chloride. A second lot of ammonium chloride is now added and the heating repeated until no more fumes are evolved. As some of the calcium sulphate may thus be converted into calcium chloride, a drop of sulphuric acid is added to reconvert this to sulphate. The crucible is then strongly heated, cooled in a desiccator, and weighed. The weight of the residue, consisting of anhydrous calcium sulphate, is multiplied by 1.26 to give the corresponding weight of the dihydrate, in which form the calcium sulphate is present in the antimony sulphide.

TESTS ON CARBON BLACK.

Acetone Extract.

Carbon blacks, especially lamp-blacks, may contain oily or greasy matter derived from the raw materials used in their manufacture. The amount of such matter is determined by acetone extraction. 2 gm. of the black are weighed out into a paper extraction thimble, and extraction is carried out with acetone in the manner already described under "Raw Rubber."

Ash.

The mineral matter present as an impurity in carbon black is determined by burning off about 2 gm. of the black in a crucible and weighing the incombustible residue.

TESTS ON LITHARGE.

Acid-insoluble Impurities.

50 gm. of the litharge is boiled with 400 c.c. of 6 per cent. nitric acid and the liquid is filtered hot through a tared Gooch crucible containing a pad of asbestos. The residue on the filter is

thoroughly washed, and the crucible and contents dried at 200 to 400° C. for one hour and weighed to determine the weight of the residue.

Lead Dioxide.

Lead dioxide, being an oxidising agent, causes rubber to "age" or perish, so that it is important that litharge for use in rubber should be substantially free from this impurity.

100 gm. of litharge is treated with hot 50 per cent. acetic acid till solution is substantially complete and the liquid is strongly acid; the mixture is then filtered hot. The wet filter paper and residue, containing the lead dioxide, is ground in a glass mortar with 40 c.c. of a saturated solution of sodium acetate in 5 per cent. acetic acid and exactly 25 c.c. of N/10 sodium thiosulphate solution. The excess of thiosulphate is then titrated with N/10 iodine solution, using starch as indicator in the usual way. If x c.c. of iodine is used, the weight of lead dioxide present in the sample is $(25 - x) \times 0.0119$ gm.

TESTS ON LITHOPONE.

Lithopone consists essentially of zinc sulphide (about 30 per cent.) and barium sulphate (about 70 per cent.), but small amounts of zinc oxide are usually present. The zinc sulphide is the active pigmentary constituent.

Zinc Oxide.

1 gm. of the lithopone, previously dried to constant weight at 110° C., is treated with 50 c.c. of 1 per cent. acetic acid at room temperature for four hours and the mixture filtered through a sintered glass crucible, previously dried at 110° C. and weighed. The solid in the crucible is well washed with hot water, and the crucible and contents then dried to constant weight at 110° C. The difference between the weight of the residue (A) and the original sample represents zinc oxide.

Any acid-soluble adulterants, such as whiting, would be included in this loss in weight, but such adulterations are now rare. If a high acid-soluble content suggests adulteration, the zinc oxide content can be determined by estimating the zinc in the acid filtrate by any recognised method.

Acid-Insoluble Matter.

The contents of the crucible are washed

into a beaker and treated with 10 c.c. of concentrated hydrochloric acid to dissolve the zinc sulphide. The mixture is diluted, heated, and filtered through the same crucible, which is then washed, dried, and weighed as above. The residue (B) represents barium sulphate, plus any acid-insoluble adulterants, such as clay.

If the lithopone is free from adulterants, the difference between A and B represents zinc sulphide. If adulteration is suspected, the zinc sulphide may be determined directly by estimating the zinc in the hydrochloric acid filtrate.

TESTS ON ZINC OXIDE.

The impurities generally looked for in zinc oxide are acid-insoluble matter and lead compounds, the latter being harmful because during vulcanisation with sulphur the black lead sulphide formed may spoil the colour of the rubber.

10 gm. of the zinc oxide is treated with 50 c.c. of concentrated hydrochloric acid and the whole evaporated to dryness, the residue taken up with water and a few drops of hydrochloric acid, and filtered. If any insoluble matter remains on the filter it is washed with hot water and the filter paper dried, ignited in a tared crucible, and the latter weighed to determine the amount of the acid-insoluble residue.

The filtrate is nearly neutralised with sodium carbonate and saturated with hydrogen sulphide. A dark precipitate or coloration indicates the presence of lead. To determine the amount quantitatively, the precipitate is filtered off and washed; the filter paper is dried and carbonised by careful heating in a large crucible. A few drops of concentrated nitric acid are added and the crucible warmed gently to expel the acid; this is repeated if necessary till the residue is white. A few drops of sulphuric are now added, the excess expelled by heating, and the crucible weighed. The residue consists of lead sulphate; each milligram corresponds to 0.0068 per cent. of lead in the sample.

A colorimetric method for determining very small amounts of lead consists in dissolving 1 gm. of the zinc oxide in 5 c.c. of concentrated hydrochloric acid and 5 c.c. of water, and making the solution alkaline by adding 5 c.c. of ammonia solution (0.880 density). Hydrogen sulphide is passed through the liquid till all

the zinc is precipitated. If lead is present the precipitate will be darkened by the black lead sulphide. To determine the amount of lead, the solution is transferred to a Nessler glass and made up to 50 c.c. An exactly similar solution ("control") is now made up from A.R. zinc oxide. To this is added, from a burette, a dilute solution of lead acetate (1.83 gm. of $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ per litre) until the colour of the "control" mixture exactly matches that of the sample under test. Each c.c. of lead acetate solution used represents 0.001 gm. of lead.

TESTS ON SULPHUR CHLORIDE.

The chief impurities to be looked for in sulphur monochloride are free sulphur, which in small amounts (say, below 5 gr. per 100 c.c.) is not harmful, and sulphur dichloride, SCl_2 , which is very harmful.

Specific Gravity.

This is most easily determined by a hydrometer in the usual way. The specific gravity of pure sulphur monochloride is 1.69.

Distillation Test and Free Sulphur Determination.

50 c.c. is distilled from a 100 c.c. distilling flask fitted with a thermometer having its bulb opposite the end of the side tube, the distillate being collected in a graduated cylinder. This operation, being familiar to all chemists, need not be described in detail. At least 95 per cent. of the liquid should distil over between 130° and 140°C. , the boiling point of pure sulphur monochloride being 137°C.

The residue in the flask is washed out into a weighed CO_2 flask with carbon disulphide, the latter distilled off, and the flask and contents dried at 110°C. and weighed; the residue represents free sulphur.

Total Chlorine.

The presence of sulphur dichloride is best detected by estimating the total chlorine content, pure sulphur monochloride contains 52.5 per cent. chlorine, a higher figure indicating the presence of the dichloride.

About 5 gm. is weighed out and made up to 100 c.c. with dry benzene. 10 c.c. of this solution is pipetted out into a flask containing 25 c.c. of N alcoholic potassium hydroxide solution. The mixture is heated on a water-bath for one hour,

the benzene and alcohol distilled off, and the flask and contents dried at 110°C. 100 c.c. of water is added and the liquid made slightly acid with nitric acid; sulphide-sulphur is precipitated by adding 10 c.c. of 10 per cent. copper sulphate solution, and the liquid filtered. The chlorine is determined in the filtrate in the usual way by adding silver nitrate solution and weighing the precipitate of silver chloride.

TESTS ON FABRICS.

Fabrics, especially if dyed or printed, are liable to contain traces of copper and manganese compounds, which are very harmful to the rubber proofing applied in making waterproof fabrics. Oily or greasy materials, often used in textile processing, must also be tested for, as they are harmful to the rubber.

Copper.

10 gm. of the fabric, cut in pieces and contained in a silica basin, is moistened with 2 c.c. of concentrated nitric acid, and 10 c.c. of concentrated sulphuric acid is added. The whole is cautiously evaporated to dryness and the charred residue incinerated. The ash is boiled for ten minutes with a mixture of 15 c.c. of 25 per cent. nitric acid and 15 c.c. of 20 per cent. sulphuric acid. The liquid is filtered, the filtrate evaporated to small bulk, and excess of ammonia added, if a precipitate forms, this is filtered off. A blue coloration in the liquid indicates the presence of copper.

Manganese.

10 gm. of the fabric is incinerated in a silica basin. The ash is dissolved in 35 c.c. of 30 per cent nitric acid, or if any unburnt carbon remains with the ash, it is preferable to take up with 25 c.c. of 10 per cent. sulphuric acid, filter, and add 5 c.c. of 30 per cent. nitric acid to the filtrate.

A little manganese-free lead dioxide is added to the acid liquid, followed by a few drops of silver nitrate solution to precipitate chlorides. The mixture is then boiled for five minutes; development of a pink colour indicates the presence of manganese.

Oil and Grease.

This is determined by extraction with acetone, in exactly the same way as for carbon black (see above).

FERTILISERS AND FEEDING STUFFS

By V. R. GREENSTREET, F.I.C.

MODERN agriculture finds no place for rule of thumb methods. Chemical control is now as essential to agriculture as it is to other great industries. Chemistry bears four important relationships towards commercial agriculture, namely, to ensure that the fertilisers, the feeding stuffs and the pest and disease preventives are of correct composition and free from adulteration.

Since it is rarely possible for the farmer to undertake the chemical analysis of his purchases it is compulsory for the seller to quote certain analytical data in respect of fertilisers and feeding stuffs.

FERTILISERS.

Nitro-Chalk.

Nitro-chalk is an intimate mixture of ammonium nitrate and the calcium carbonate which occurs as a by-product in the manufacture of ammonium sulphate from synthetic ammonia. The manufacture of synthetic ammonium sulphate and nitro-chalk are closely allied. Ammonia gas mixed with a definite proportion of air is passed over a heated platinum gauze. Reaction occurs and the gases combine according to the following equation: $\text{NH}_3 + 2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O}$.
(nitric acid and water)

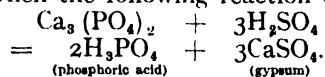
Further ammonia is passed into the nitric acid to produce ammonium nitrate: $\text{HNO}_3 + \text{NH}_3 = \text{NH}_4\text{NO}_3$.

The resulting ammonium nitrate solution is inspissated and well mixed with dried calcium carbonate from the ammonium sulphate plant (see page 20). While still hot, the resulting slurry is sprayed from the top of a tall tower. Rapid cooling occurs and the drops solidify in the form of granules. The granular nature of nitro-chalk and other modern fertilisers simplifies distribution in the field and is a feature much appreciated by farmers.

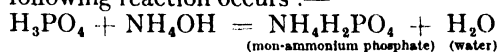
Compound Granular Fertilisers.

Phosphate rock, after grinding in ball mills, is treated with strong sulphuric

acid, when the following reaction occurs:



The gypsum is precipitated and filtered off on rotary filters. Ammonia is added to the phosphoric acid solution, when the following reaction occurs:—

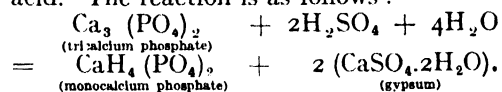


The addition of the ammonia is carefully controlled until the acidity corresponds with that of mon-ammonium phosphate. Mon-ammonium phosphate contains 62 per cent. of phosphoric acid and 12 per cent. of nitrogen, proportions which have been found to be unsuitable for fertilisers. It is usual, therefore, to raise the nitrogen content by the addition of ammonium sulphate solution, followed by subsequent evaporation and crystallisation to a granular form.

By mixing mon-ammonium phosphate and ammonium sulphate in equal parts, the phosphoric acid content of the resulting granules is reduced to about 31 per cent. and the nitrogen content is raised to nearly 17 per cent.

Superphosphate.

Agricultural superphosphate of lime consists of a mixture of gypsum and monocalcium phosphate and is manufactured by treating rock phosphate with sulphuric acid. The reaction is as follows:—



The original tricalcium phosphate is insoluble in water and ammonium citrate, while the monocalcium phosphate produced will dissolve in both solvents. The phosphoric acid is thus rendered "available" for plant life.

The manufacturing process consists of treating finely divided rock phosphate with sulphuric acid. A fine state of division of the rock is essential in order to achieve intimate contact with the acid. The

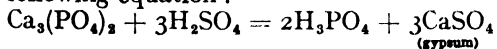
grinding mill is, therefore, an important feature of a superphosphate factory. The rock often receives a preliminary crushing and is finally ground to pass a 100-mesh sieve.

The ground rock is treated with a pre-determined amount of sulphuric acid of strength 50 to 52° Bé (chamber acid) and the mixture agitated vigorously with a mechanical stirrer. The chemical reaction raises the temperature and causes the mass rapidly to stiffen. In two or three minutes the mixture is discharged into a "den," otherwise an undue strain is imposed upon the machinery and it may be impossible to remove the whole charge.

The reaction is allowed to proceed in the "den" situated below the mixer, where the reaction raises the temperature to about 100° C., and where carbon dioxide, steam and gaseous fluorine compounds are evolved. After an interval of 24 hours, the mass is transferred to a storage pile, where it is allowed to remain for several weeks. During this period the proportion of available phosphoric acid tends to increase. Storage in large piles must not be too protracted, however, or the mass may tend to become cemented together.

Double Superphosphate.

Double superphosphate has the advantage over normal superphosphate of reducing transport costs. It is produced by treating rock phosphate with ortho-phosphoric acid instead of sulphuric acid. The phosphoric acid required is prepared from ground rock phosphate by treating it with sulphuric acid according to the following equation:—



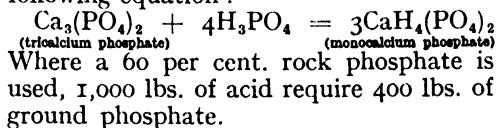
Phosphoric acid manufactured from rock phosphate is contaminated with calcium phosphate, iron, aluminium, fluorine, arsenic and lead, but these impurities are not deleterious for double superphosphate. High-grade phosphoric acid obtained by treating bones with sulphuric acid is used for making baking powder, etc., and its high cost militates against its use in the fertiliser industry.

Rock phosphate ground to pass a 60-mesh sieve is stirred with water and sulphuric acid in lead, or acid-proof lined, vats for three to five hours. The product is filtered through a filter press, or a

vacuum filter. The calcium phosphate residue should contain no more than 1 per cent. of available phosphoric acid on a dry basis.

The dilute phosphoric acid produced needs to be concentrated by evaporation. This is performed in lead-lined vessels by the aid of lead steam coils. It is important to prevent the temperature rising above 150° C., at which point ortho-phosphoric acid is converted into pyrophosphoric acid. At atmospheric pressure phosphoric acid can only be concentrated to 50° Bé (44 to 47 per cent. P_2O_5).

The concentrated phosphoric acid is run into a mixer and a weighed amount of ground rock phosphate added. The reaction proceeds in accordance with the following equation:—



After thoroughly mixing for a few minutes, the product is discharged to a den, as in the manufacture of normal superphosphate and where the reaction is allowed to proceed.

Since double superphosphate contains no calcium sulphate to absorb excess water, it needs to be dried mechanically. This is usually carried out in a rotary drier, followed by disintegration, screening and bagging.

Basic Slag.

Basic slag is a by-product of the process of manufacturing phosphorus-free steel from iron containing this element. Basic slag may be made in two ways, i.e., Gilchrist's and Thomas's modification of the Bessemer chamber process and Siemens' open hearth process. In each case the reaction depends upon the affinity for phosphorus of the basic lining of the furnace, in addition to which limestone may be mixed with the charge.

Bessemer slag is made from pig iron and open hearth slag from a combination of iron ore and pig iron. In the former case a pig iron rich in phosphorus is desirable, since the oxidation of the phosphorus helps to raise the temperature. In the manufacture of open hearth slag the heat necessary is largely supplied by producer gas and a high-phosphorus ore is disadvantageous. Moreover, a greater

quantity of slag is produced. Consequently, Bessemer slag is richer in phosphorus than open hearth slag.

It has been proved that the fertilising value of basic slag is related to the solubility of its phosphoric acid in 2 per cent. citric acid. The highest grade Bessemer slag contains 17 per cent. of phosphoric acid soluble in citric acid, out of a total of 20 per cent. phosphoric acid. Open hearth basic slag contains no more than 12 per cent. of phosphoric acid soluble in citric acid, out of a maximum total of 14 per cent. phosphoric acid.

The grinding necessary in order to enable basic slag to pass the standard sieve of 10,000 holes per square inch is usually carried out in a ball mill.

A mixed fertiliser, known as potassic slag, is made by grinding together basic slag and kainit.

Calcium Cyanamide.

Calcium cyanamide is produced when calcium carbide is heated in a stream of nitrogen. Finely ground calcium carbide is passed through a heated revolving drum together with excess of nitrogen when the following reaction occurs:—

$$\underset{\text{(calcium carbide)}}{\text{CaC}_2} + \text{N}_2 = \underset{\text{(calcium cyanamide)}}{\text{CaCN}_2} + \text{C}$$

The absorption of nitrogen commences at 700° C., but reaches its maximum at 1,100° C. The process is carried on continuously and the reaction is exothermic, thus effecting an economy in the amount of heat to be supplied.

Unfortunately, the reaction does not proceed strictly according to the equation. In practice, considerably more carbon is liberated and it is considered satisfactory if the nitrogen content does not fall below 15.5 per cent.

Nitrate of Lime.

Nitrate of lime has been largely superseded by nitro-chalk, which is a more efficient fertiliser and more convenient to handle. Nitrate of lime is manufactured by passing nitrogen peroxide through absorption towers containing milk of lime. The solution is evaporated and the resulting calcium nitrate suffers from the disadvantage of marked hygroscopicity.

METHODS OF ANALYSIS APPLICABLE TO FERTILISERS.

Potash (K₂O).

In the absence of sulphates, dissolve in

water an amount equivalent to about 2 gm. of K₂O, filter if cloudy and make up to 500 ml. Transfer 50 ml. to a small glass basin, add 7 ml. of pure 20 per cent. HClO₄ solution and evaporate to white fumes. Add a little hot water and a few drops of HClO₄ solution and again concentrate to white fumes. When cool, thoroughly mix in 20 ml. of diluted alcohol of density 0.812-0.816, allow the precipitate to settle and filter through a sintered glass Gooch crucible No. 3. Wash the precipitate by decantation with diluted alcohol (saturated with KClO₄), dry at 100° C and weigh as KClO₄.

Sulphates interfere with the precipitation of KClO₄ and if present must be removed by boiling the weighed portion with 300 ml. of water containing 20 ml. of HCl and then adding BaCl₂ drop by drop to the boiling solution until all the H₂SO₄ is precipitated. Cool, make up to 500 ml., filter and evaporate to dryness 50 ml. of the filtrate. Moisten with conc. HCl, evaporate to dryness, treat with a little dilute HCl and filter if cloudy. The solution is now free from sulphates and the potash may be precipitated with HClO₄ as already described.

Phosphates, iron, manganese and organic compounds also interfere with the precipitation of KClO₄ and must be removed by *gentle* incineration followed by heating for 10 mins. with 10 ml. of conc. HCl and then boiling with 300 ml. of water. Filter, boil and add powdered Ba(OH)₂ until slightly alkaline. Cool, make up to 500 ml. in a graduated flask and filter. Treat 250 ml. with NH₄OH and excess NH₄CO₃, boil and add (NH₄)₂C₂O₄, cool, make up to 500 ml. and filter. Evaporate 100 ml. to dryness and expel ammonium salts by heating to not more than 700° C. Moisten the residue with conc. HCl and filter. The solution is now free from sulphates, phosphates, iron, manganese and organic compounds and is ready for the determination of potash with HClO₄ as already described.

Determination of Nitrogen.

Organic and ammoniacal nitrogen is determined by Kjeldahl's method.

In the case of ammonium salts a direct distillation into standard acid is all that is required. If organic matter is present a direct distillation with 5 gm. of magnesium oxide instead of caustic alkali will

serve to determine the amount of ammonium salts. Use of caustic alkali would liberate some ammonia from the organic matter. If CaCO_3 is present, the interference of CO_2 may be prevented by first dissolving the substance in HCl .

For the determination of nitrogen in salts of nitric acid, in the absence of organic matter treat a solution of the substance with six times its weight of Devada's alloy, add excess of caustic alkali and connect the flask with the distillation apparatus. After $\frac{1}{2}$ hour, when the reduction of the nitrate to ammonia will be complete, distil as already described. In the presence of organic matter, reduce the nitrate in 1 gm. or more of the substance with 10 gm. of reduced iron and 20 ml. of H_2SO_4 (density, 1.35) in 50 ml. of water. Close the flask with a rubber bung provided with a thistle funnel containing glass beads. Let stand until effervescence ceases and then boil for 5 mins.; wash the condensed liquid from the beads back into the flask, reboil for a further 3 mins. and rewash the beads. Finally add 5 gm. of magnesium oxide and distil off the ammonia as already described.

On account of their liability to contain traces of nitrogen compounds, carry out a blank determination on each batch of the different reagents used and make the correction in the analysis that is found necessary.

Determination of Phosphoric Acid (P_2O_5).

Soluble phosphoric acid is determined by shaking not less than 20 gm. of the substance with 800 ml. of water for half-hour. Make up to 1 litre and filter. Boil 50 ml. of the filtrate with 20 ml. of conc HNO_3 , add molybdic acid solution in excess (100-150 ml.) and maintain the mixture at 70°C . for a quarter of an hour. Cool, filter and wash the precipitate with 1 per cent. HNO_3 solution. Test the filtrate and washings for freedom from P_2O_5 . Dissolve the precipitate in about 100 ml. of cold NH_4OH solution (2 per cent.), heat nearly to boiling, add excess of magnesia mixture (15-20 ml.) drop by drop with constant stirring. After an interval of not less than four hours, filter, wash the precipitate with 2 per cent. NH_4OH until free from chlorides, dry, ignite at 900°C . and weigh as magnesium pyrophosphate.

1 gm. magnesium pyrophosphate

($\text{Mg}_2\text{P}_2\text{O}_7$)

= 0.64 gm. phosphoric acid.

The required molybdic acid solution is prepared in the following manner:—Dissolve 125 gm. of molybdic acid in 100 ml. of water and 300 ml. of 8 per cent. ammonia solution, add 400 gm. ammonium nitrate, make up to 1 litre and mix with 1 litre of nitric acid (density, 1.19). Keep warm for 1 day and filter.

The magnesia mixture is prepared in the following manner:—Dissolve 110 gm. of magnesium chloride and 140 gm. of ammonium chloride in 1,300 ml. of water, mix with 700 ml. of 8 per cent. ammonia and filter after 3 days.

The 8 per cent. ammonia solution must be of density 0.967 and is prepared by mixing 200 ml. of .880 ammonia with 600 ml. of water. The 2 per cent. ammonia solution is prepared from the 8 per cent. solution by mixing 100 ml. with 300 ml. of water.

For the determination of total phosphoric acid digest the substance with conc. H_2SO_4 until all organic matter is destroyed. After cooling and dilution, filter, wash the precipitate and redigest it with H_2SO_4 in order to extract the last traces of P_2O_5 . Bulk the two filtrates and determine P_2O_5 in the manner already described.

Analysis of Limes.

The following method serves to determine the total amount of lime in the form of CaO and Ca(OH)_2 . After rapidly grinding and sieving through a 0.2 mm. sieve transfer 5 gm. to a stoppered litre bottle. Moisten with 10 ml. of neutral alcohol (to prevent caking), add 490 ml. of a neutral 10 per cent. sugar solution and shake for not less than 4 hours. Filter and titrate 50 ml. with $\text{N}/2$ HCl using phenolphthalein.

For the determination of calcium oxide (CaO) dissolve the finely ground sample in dilute HCl , filter, transfer 50 ml. of the solution containing about 0.02 gm. CaO to a 400-ml. beaker, add 2 drops phenolphthalein and conc. ammonia drop by drop from a burette until a permanent precipitate occurs and a pink colour is *just* formed. Add 3 ml. of 2N oxalic acid, 200 ml. of hot water and stir. Boil and add 50 ml. of saturated ammonium oxalate and continue boiling for half hour. Cool and filter at the pump through sintered glass Gooch crucible No. 4. Wash with cold water until a test-tube

full of washings to which is added a few drops of 5 per cent. H_2SO_4 and the whole brought to the boil does not decolorise 1 drop of N/20 KMnO_4 . Transfer the crucible to a 600 ml. pyrex beaker and cover with 5 per cent. H_2SO_4 , boil until the precipitate has dissolved and imme-

diately titrate with N/20 KMnO_4 .
1 ml. N/20 KMnO_4 = 0.0014 gm. CaO .

FEEDING STUFFS.

Modern feeding stuffs fall into two categories (1) Animal and vegetable matter, either raw, cooked or by-products from the

	OIL.		PROTEIN.		CRUDE FIBRE.		CARBO-HYDRATE.		VALUE.	SOURCE.
	Per cent.	D.C.*	Per cent.	D.C.	Per cent.	D.C.	Per cent.	D.C.		
WHEAT, whole, ground										
or crushed	1.6	70	12.6	80	1.8	60	68.0	83	95	—
Broad bran	2.8	72	15.0	75	9.9	33	56.3	66	77	Milling
Fine bran	2.8	72	14.2	75	8.7	33	58.1	66	79	by-products.
Plate bran	2.0	72	18.7	75	9.6	33	53.5	66	80	do.
Coarse pollards ..	3.0	72	14.5	75	7.8	33	57.9	66	80	do.
Weatings	2.6	72	13.9	75	4.5	33	64.6	66	83	do.
Middlings, special plate	4.0	80	20.0	80	3.9	36	57.5	75	90	do.
do. plate	4.1	80	17.5	80	7.3	36	54.8	75	86	do.
do. Dutch	4.0	80	19.1	80	5.5	36	57.3	75	86	do.
do. Italian	4.1	80	15.0	80	1.4	36	65.5	75	90	do.
Low grade flour ..	3.3	92	14.5	90	2.2	100	67.0	80	100	do.
RYE, ground	1.8	64	11.4	84	2.0	55	69.3	95	100	—
do. flour	0.8	80	5.5	80	0.2	20	80.9	75	100	—
BARLEY meal	2.3	49	11.6	75	5.1	12	66.3	89	99	—
OATS, Chilean crushed	5.5	70	7.7	80	9.0	20	63.7	75	95	—
do. Sussex ground	5.0	70	11.5	80	11.5	20	57.1	75	93	—
MAIZE meal	7.1	74	9.6	84	2.4	41	66.6	94	97	Corn-flour
do. flaked	2.1	45	10.1	90	0.7	33	74.4	95	100	by-product.
do. gluten feed ..	3.0	79	22.5	83	6.1	70	57.7	86	100	Cooked and
do. do. meal	4.6	94	35.6	85	2.0	—	47.5	89	100	rolled.
RICE meal	13.3	76	11.8	58	6.6	20	46.0	78	100	Distillery
do. bran	7.1	70	12.3	60	1.4	10	57.9	75	95	by-products.
PEA meal	1.4	49	10.6	90	0.7	70	70.1	96	98	Milling
LINSEED	36.3	86	24.4	91	5.4	60	23.1	55	99	by-products.
do. cake	8.6	80	26.3	86	8.7	32	38.2	85	97	—
do. extracted meal	3.0	95	35.8	84	8.9	54	34.0	82	96	Oil mill
PALM KERNEL cake ..	7.8	78	18.7	69	13.5	36	45.2	77	100	do.
do. extracted meal	0.4	78	21.1	70	15.9	36	50.0	77	100	do.
SOYA cake	7.1	92	42.3	78	5.1	40	25.7	70	97	do.
do. meal	1.1	90	47.1	80	5.1	40	31.7	70	97	do.
GROUND-NUT cake										
decorticated	7.3	80	44.8	70	7.3	40	24.3	80	98	do.
do. undecorticated	9.2	90	30.1	80	23.0	9	21.7	84	86	do.
COTTON-SEED cake										
decorticated	10.0	80	38.9	70	8.4	40	27.4	80	97	do.
do. undecorticated	4.5	80	23.5	72	22.8	18	31.1	57	84	do.
COCONUT cake	9.8	77	20.8	78	11.1	63	41.5	83	100	do.
TAPIOCA flour										
decorticated	0.4	70	2.6	85	1.8	30	84.7	95	100	Milled
do. undecorticated	0.3	80	3.2	80	2.4	25	80.9	95	99	roots.
SUGAR-BEET PULP, plain	0.5	30	9.0	65	18.2	90	59.2	93	87	Sugar
do. molassed	0.4	25	10.7	60	15.0	90	58.3	92	87	by-product.
TREACLE meal	0.4	—	9.6	50	7.2	20	71.3	90	87	do.
MILK, dried, whole ..	17.1	95	25.0	96	—	—	46.5	98	100	—
do. do. separated	1.1	93	29.1	96	—	—	53.5	98	100	Cream
BLOOD MEAL	0.1	—	78.8	72	—	—	—	—	100	by-product.
MEAT AND BONE MEAL										
40 per cent.	10.4	86	37.6	97	—	—	—	—	100	Abattoir
do. 45 per cent. ..	12.6	86	42.4	97	—	—	—	—	100	by-products.
do. 50 per cent. ..	3.9	86	49.9	97	—	—	—	—	100	do.
MEAT MEAL, 60 per cent.	3.5	98	58.1	93	—	—	—	—	100	do.
do. 65 per cent. ..	9.5	98	59.2	93	—	—	—	—	100	do.
WHALE MEAT MEAL ..	11.1	90	53.8	91	—	—	—	—	100	Whale-oil
FISH MEAL, white ..	3.8	76	60.8	90	—	—	—	—	100	by-product.
do. Canadian	3.9	76	63.5	90	—	—	—	—	100	Fishing

D.C. = Percentage digestibility coefficient.

manufacture of human food or other commodities, and (2) Mineral supplements which are compounded expressly for cattle feeding.

In view of their very great number and diversity and since Chemistry does not enter very largely into their manufacture it is proposed to present feeding stuffs in tabular form. The accompanying table gives the composition and derivation of typical samples of the principal feeding stuffs at present on the English market together with the digestibility coefficients of their oil, protein, fibre and carbohydrate, and their "value" numbers.

It is compulsory for the total oil, protein and fibre content of certain feeding stuffs to be declared and the following are the methods of analysis to be employed. The analysis is always carried out on material which has been ground to pass a 1 millimetre sieve.

Determination of Oil.

Dry 10 gm. for 2 hours at 100° C., transfer to an extraction thimble in a Soxhlet apparatus and extract with petroleum ether (boiling point, 40-60° C.) for 3 hours. Remove the thimble, dry and grind the feeding stuff and return it to the extraction apparatus. Continue the extraction for 1 hour, filter the solvent into a weighed flask (thoroughly washing the extraction flask and filter paper with petroleum ether), distil off the solvent, dry the extracted oil for 3 hours at 100° C. and weigh.

Determination of Protein.

Digest 1 gm. with conc. H_2SO_4 , Na_2SO_4 and CuSO_4 as described under the determination of organic and ammoniacal nitrogen in fertilisers. After cooling and dilution make up the volume to 250 ml. in a graduated flask. Distil 50 ml. with excess of caustic soda into 20 ml. of decinormal acid and finally titrate with decinormal soda, using alizarin red S indicator. The number of millilitres of acid neutralised by the ammonia liberated in the distillation multiplied by 4.375 represents the percentage protein content of the feeding stuff under analysis.

Determination of Crude Fibre.

Treat 2 gm. with three successive portions of petroleum ether in a litre flask or beaker. When all the solvent has

evaporated add 200 ml. of a 1.25 per cent. solution (boiling) of H_2SO_4 and boil for 30 minutes. Maintain the original volume by the addition of water and wash particles from the sides of the vessel. While hot filter at the pump and wash free from acid with boiling water. Transfer the residue to the original vessel, add 200 ml. of a 1.25 per cent. boiling solution of NaOH and boil continuously for 30 minutes. Filter at the pump, wash with boiling water, then with 1 per cent. HCl and again with boiling water until free from acid. Wash with alcohol and ether and transfer the crude fibre to a silica dish. Dry to constant weight, weigh, ignite at a dull red heat and reweigh. The difference between the two weighings represents the weight of crude fibre in 2 gm. of the feeding stuff.

Determination of Sugar.

In the case of sugar by-products sold as feeding stuffs it is compulsory for the sugar content to be declared. The method of determining sugar is as follows. Grind 10 gm. with successive amounts of water, 200 ml. in all, and transfer to a 250 ml. graduated flask. Shake the flask and, if the contents are highly coloured, treat with basic lead acetate followed by sodium sulphate. Make up to 250 ml., filter and invert 50 ml. with 5 ml. of 38.3 per cent. HCl at 70° C. for 10 mins. Cool, neutralise with sodium carbonate, make up to 100 ml. and filter. Determine the sugar content by either the gravimetric or volumetric processes (described in the article on sugar refining).

Determination of Salt.

In the case of white fish meal it is illegal for the salt content to be above 4 per cent. The method of determining salt in fish meal is as follows.—Heat 5 gm. with pure lime until the organic matter is completely charred. Extract the residue with water, make up to 250 ml. and filter. Treat 50 ml. with decinormal silver nitrate in slight excess, stir, filter and wash the precipitate. To the combined filtrate and washings add 5 ml. of a saturated solution of ferric ammonium alum, a few ml. of nitric acid free from lower oxides of nitrogen and titrate the excess of silver with decinormal thiocyanate solution until a permanent light brown colour occurs. 1 ml. decinormal silver nitrate equals 0.00585 gm. of sodium chloride.

Determination of Iodine.

Boil with water to extract soluble salts, filter and boil for 10 mins. 10 mls. of the solution with 1 ml. of double normal HCl and 1 ml. of saturated bromine water. Cool to 10° C. and add 1.5 ml. of syrupy phosphoric acid and 0.2 gm. of KI. After standing in the dark for 3 mins. titrate with 0.004 N sodium thiosulphate. Add starch and finish the titration, allowing an interval of 1 min. between drops. Before use, standardise the thiosulphate solution against pure KI.

Determination of the Starch Equivalent of a Feeding Stuff.

The starch equivalent of a feeding stuff is one of the principal measures of its feeding value. Many reputable manufacturers of compound feeding stuffs declare the starch equivalent. The starch equivalent of a compound feeding stuff cannot be determined without a knowledge of the proportions and composition of the various ingredients.

Determination of Amides.

Before proceeding to determine the starch equivalent (S.E.) of each ingredient it is necessary to determine its content of amides. Amides are determined as follows:—Boil 1 gm. of the feeding stuff with 50 ml. of water for 30 mins. Cool, add 50 ml. of saturated copper acetate and filter off the precipitate as soon as it settles. Wash the precipitate with cold water, dry and determine its protein content by Kjeldahl's method. The difference between this figure and the total protein content represents amides.

The S.E. is calculated in the following manner:—Multiply the percentage of total protein, oil, fibre and carbohydrates by their respective digestibility coefficients. This gives the proportions of digestible protein, oil, fibre and carbohydrates respectively. From the proportion of digestible protein subtract the proportion of amides and multiply the difference by 0.94. Add the resulting figure to the proportion of digestible oil multiplied by 2.41. To the sum of these two add the proportions of digestible fibre and carbohydrates. This total is the gross starch equivalent. To reduce the gross starch equivalent to the net starch equivalent, multiply the former by the value figure corresponding to the feeding stuff under

consideration and divide the amount by 100. The S.E. of a compound feeding stuff is the sum of the starch equivalents of the constituents expressed as a percentage of the whole.

The Adulteration of Feeding Stuff.

Serious adulteration of feeding stuffs is but rarely practised, for the accidental or deliberate substitution of a cheaper ingredient can usually be discovered by microscopic examination. The presence of castor seed or mustard, however, is attended by such disastrous consequences to stock that it is important to be able to prove their complete absence.

Determination of Castor Seed.

To determine castor seed, treat 250 gm. of the cake in a 2-litre vessel with 100 ml. conc. HCl, dilute with boiling water and stir. After 30 mins. allow the mixture to settle for a short time, pour off the top liquor and fill the vessel with boiling water which after settling pour off. Refill and decant twice. Add 30 gm. of NaOH in water, dilute with boiling water and wash as before. Make up 30 gm. of bleaching powder to a cream with 500 ml. of cold water, stir frequently, allow to settle and pour the supernatant liquor upon the residue in the vessel. Upon standing overnight the husks of most oil seeds are sufficiently bleached to form a sharp contrast with fragments of the testa of castor oil seeds, which are so far unaffected as to lose only their delicate thin mottled outer membrane and remain as dark brown angular brittle fragments which appear black in water and are easily recognisable under the microscope. To separate these particles pour the contents of the vessel portion by portion into a large white photographic dish and wash away bleached particles with successive quantities of water. Portions of castor-oil seed husk, being heavy, remain at the bottom. The dry weight of the particles multiplied by five represents the approximate original weight of castor-oil seeds.

Detection of Mustard Seeds.

Mix in a bottle 10 gm. of finely ground meal to a paste with cold water. Cork the bottle and stand in a warm place for 2 hours. Cool and open, when the presence of mustard is indicated by the smell and taste.

PRINTING INKS

PART IV.—TESTING OF INKS

By G. L. RIDDELL, Ph.D., A.I.C.

Director, The Printing Industry Research Association

SUCH tests as are performed on printing inks are generally empirical and made in comparison with inks whose performance is known. The development of adequate scientifically accurate methods for testing is impossible while the essential physical properties of the inks from a point of view of the various printing processes remain unknown, and the measurement of these physical properties is further complicated by the wide variations in the types of inks used in the different processes.

FINENESS OF GRINDING.

Experts are still debating whether the grinding of pigments into varnish actually reduces the particle size of the pigments or only breaks down pigment aggregates and disperses crystals in the varnish. It is probable that the maximum permissible size of particle for the production of high-class inks bears some relation to the degree of wetting of the pig-

ment by the medium, but this has never been reduced to definite figures. The pigment or pigments in an ink can be present as dispersed individual particles or flocculates of oil-wetted particles. The

presence of the latter, although sometimes giving a poor appearance to the ink if examined under the microscope, need not be feared as they are completely redispersed by the excellent distribution mechanism on the average printing machine. The presence of large individual particles and unwetted pigment aggregates should, however, be looked for as these

are liable to give trouble by wearing the printing surface and giving bad and uneven prints.

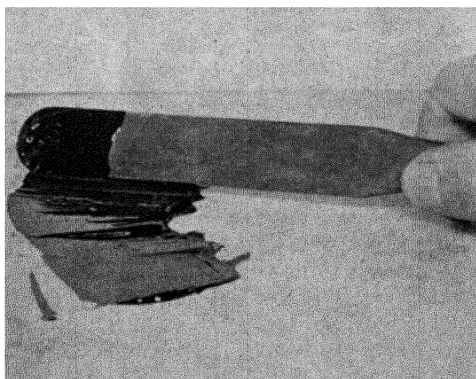
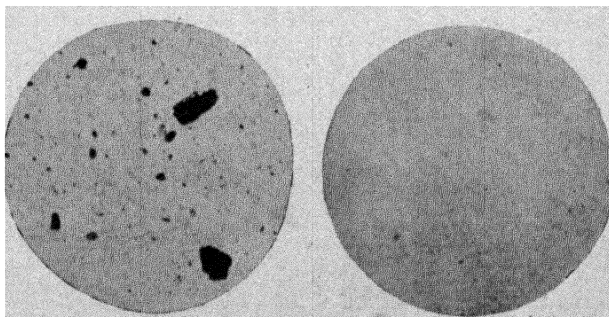


Fig. 1.—THE KNIFE TEST FOR FINENESS OF GRINDING.

Ink is spread with a knife and should appear as a uniform liquid.



PIGMENTS IN GROUND INK

That on the left is unsatisfactory. That on the right is good.

Knife Test.

Badly ground and coarse pigments are usually recognisable by spreading the ink with a knife on a slab. The ink coming from under the blade should have the appearance of a

uniform liquid, no visible particles being present. The appearance of a "grain" indicates either that the pigments have been badly ground or that pigments of large ultimate particle size of pigment are present. Certain hard substances such as the earth colours (siennas, ochres, and umbers), cheap fillers (some grades of china clay), and the inorganic salts used in paste driers almost invariably give a granular appearance to the ink. This defect cannot be eliminated in inks containing these materials. It should be noted that inks which have been stored for a considerable time at a low temperature sometimes exhibit a granular appearance, due to the crystallisation of saturated fatty materials from the varnish. This can easily be differentiated from pigment "grain" as the former can be eliminated by slight warming.

Microscopical Examination.

The cause of the granular appearance of an ink can be definitely ascertained by examining a microscope slide of the ink under $\frac{1}{8}$ -in. microscope objective. In the best type of inks, e.g., those used for fine half-tone work, the particles of pigment are usually so small that most of them are not visible under a $\frac{1}{8}$ -in. objective and this method can be used for differentiating between a high quality ink and one which is made of inferior materials or is insufficiently ground. If a number of large particles are visible it is probable that the ink will not be satisfactory. Microscope slides of printing inks are best made by rubbing a very small quantity of the ink (about 1-2 milligrams) with refined linseed oil until a uniform dispersion is obtained. The preparation of a slide by this method generally redisperses any flocculates that may have been present in the original ink. To prepare permanent slides of printing inks it is better to use as the dispersing medium a solution of Canada balsam in xylol.

TINCTORIAL STRENGTH.

The method used for determining the tinctorial strength of inks is merely comparative, the ink under test being compared with a standard ink. Actual colour measurements have, up to the present, not proved successful.

The experimental procedure is as follows. Exactly half a gram of the ink under test and 10 gm. of a standard zinc white letterpress ink of known composition and properties are weighed on to a glass slide or vegetable parchment circle. (A large supply of the zinc white ink should be kept for this reduction test in order to eliminate any possible differences between various batches.) The two inks are transferred

and mixed on a glass or marble slab with the aid of a Muller or palate knife until on spreading under the knife no streaks of colour or unevenness of tone is apparent. This procedure is repeated for the standard ink. Small quantities of the two tints thus prepared are placed in juxtaposition on a colourless glass microscope slide so that a line showing the

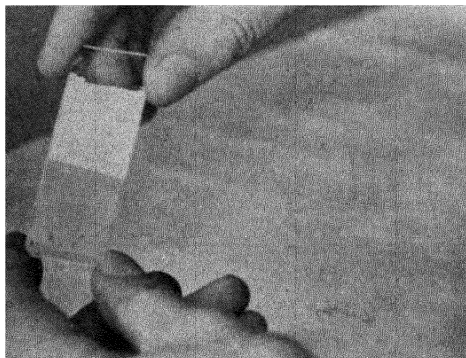


Fig. 3.—TINCTORIAL STRENGTH.

Films of the standard ink and ink under test are placed in juxtaposition on the microscope slide and viewed from the reverse side.

meeting of the two tints can be observed by viewing through the glass as in Fig. 3. The quantities used on the glass should be such that the films are opaque and they should be viewed by reflected light.

If a difference in strength is apparent a further quantity of the zinc white ink is weighed on to another piece of vegetable parchment and portions are mixed with the stronger tint until its strength is reduced to that of the weaker. In this condition the line of demarcation between the two tints on the glass is not visible. The amount of zinc white used is found by weighing the residue and the relative colour strengths of the two inks can be determined from a comparison of the degrees of reduction. For example, the weaker ink will be a 20 : 1 reduction and if 5 extra gm. of zinc white are used the degree of reduction of the stronger ink

will be 30 : 1. Thus the tinctorial value of one will be $3/2$ times the other.

It is essential that the same reducing white should be used in all tests as different whites (e.g., lead white in place of zinc white) do not always classify the same inks in the same order. This remark also holds true for the strength of the reduction, i.e., 20-1 or 50-1 should be consistently used. The sensitivity of the test, which, of course, is liable to all the personal factors, is about 5 per cent. and it is difficult to compare inks in this way if the shades are even slightly different.

TACK.

Tackiness is an important property of inks and some measure of it should be taken since paper troubles such as picking will result with too tacky inks. At present an entirely practical comparative test is adopted consisting of printing the two inks to be compared. It is usual to run up equal weighed quantities of the two inks side by side on the same machine and to get prints of each on a standard art paper. If the actual paper on which the ink is to be used is available, then the test is done with this material. Prints should be taken at various speeds on the machine, if possible corresponding to the speeds likely to be used in practice. This method, although purely rule-of-thumb, gives results fairly strictly comparable.

VISCOSITY.

Owing to the presence of a high concentration of disperse phase printing inks do not usually behave as normal liquids, i.e., the rate of shear, in general, is not proportional to the shearing stress. It is probable that there is a minimum rate of shear above which any ink will behave as a normal liquid, but this minimum would be a characteristic of the ink and would vary widely according to the type

of pigment and its concentration. The minimum shear is low for rotary news and photogravure inks and hence efflux viscometers can be used for these materials. To obtain comparative results for all kinds of inks it is thus necessary to make viscosity measurements at a constant rate of shear. No method has yet been devised for measuring the viscosity of inks at the actual rate of shear applied on printing machines so that it is usual to choose some lower but constant rate of shear at which measurement can be made. It should be pointed out, however, that it does not follow that the results will be strictly comparable at the higher rates of shear at which the inks are used.

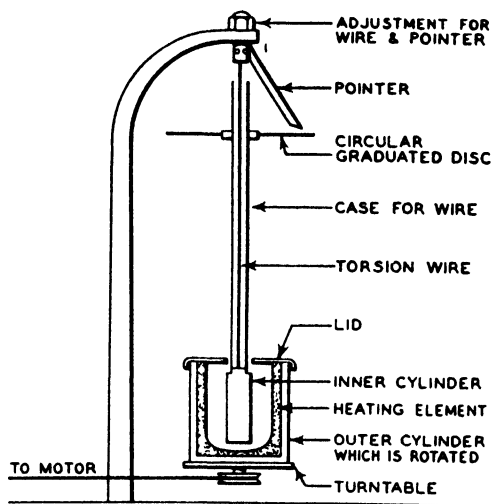


Fig. 4.—THE MACMICHAEL VISCOMETER.

The MacMichael Viscometer.

The most convenient instrument for use with inks is the MacMichael Viscometer shown diagrammatically in Fig. 4. The errors due to varying friction are avoided in the MacMichael instrument in which the inner cylinder is made to act as the bob of a torsion pendulum. The ink under test is placed in the space between the outer cup and the inner cylinder, which is attached by a torsion wire to a graduated disc. By rotating the outer cylinder at a constant speed (60 to 120 r.p.m. is convenient) the inner cylinder is caused to rotate and the annular twist imparted to the wire is read off on the scale.

The instrument should be calibrated against a varnish of high and known viscosity.

Inks which have been stored for some considerable time, especially if these contain carbon black and lithographic varnish, may have to be stirred in the instrument for some considerable time until a constant reading is obtained. This is due to the fact that old inks have a definite structure and this is only very gradually broken down by the shearing

stress applied by the rotation.

The Stormer Viscometer.

The measurement of viscosity by observation of the speed of rotation of one of two concentric cylinders rotated by means of a torque applied by a falling weight can be used where a small shearing stress is sufficient to eliminate anomalous flowing properties. The Stormer instrument is designed on this basis and can be used for news and photogravure inks.

DRYING TIME.

The following factors are known to influence the time taken for a print to become dry—temperature, atmospheric humidity, film thickness, evaporation of solvents and oxidation products, paper, irradiation. For inks which dry by oxidation and evaporation only, observations can be made of the drying of a film of ink 1-3 microns in thickness on glass. Such a film is best obtained by rolling the ink with a printer's composition roller on a piece of carefully cleaned and weighed glass and calculating the thickness from the weight, the specific

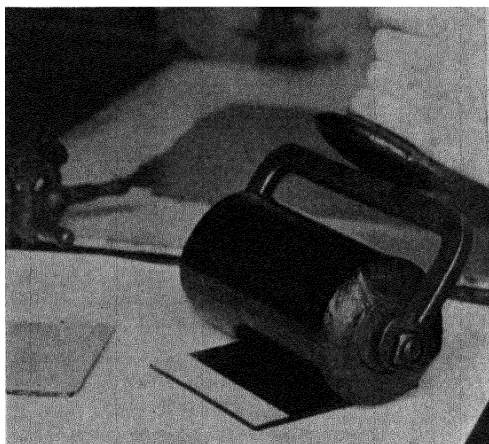


Fig. 5.—DRYING TIME (1).
Ink film is rolled on to plate glass.

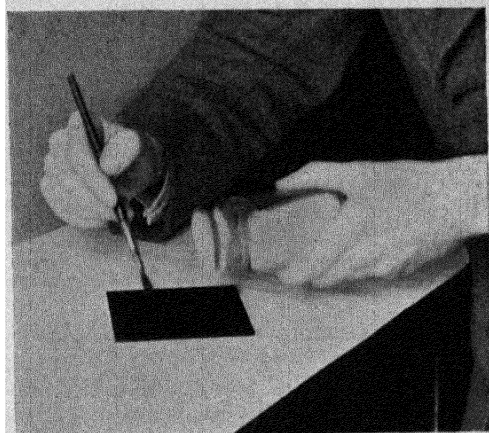


Fig. 6.—DRYING TIME (2).
Dryness of ink film is tested by sprinkling on silver sand and brushing off with camel-hair brush.

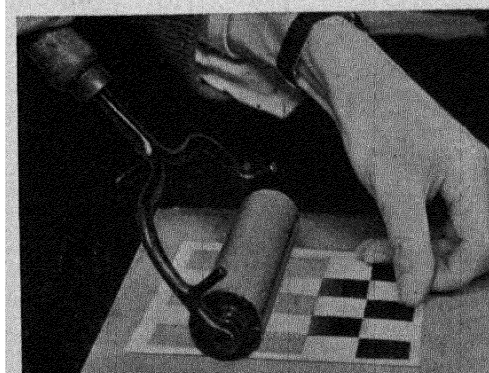


Fig. 7.—DETERMINATION OF OPACITY OF INK
BY ROLLING INK ON TO A "DRAUGHT BOARD"
TIN.

gravity having been determined. The drying time is observed by the method suggested by the British Standards Institution, i.e., applying 40-80 mesh silver sand at intervals after the film has been applied to glass and noting the time after which the sand can be removed by gently brushing with a camel-hair brush (Fig. 5 and 6). The Sanderson machine (vide Proc. A.S.T.M. 25 Pt. 2 407, 26 Pt. 2 556) is an attempt to mechanise the B.S.I. test, but like the former can only be used with inks which dry by oxidation.

For prints on paper there are two points in the drying which are of importance (a) initial set; (b) final hard drying. The time to reach the first point is important as an indication of the time required for the prints to dry sufficiently to be handled, the time for final hardness when the ink film can no longer be smeared by pressure, being in some cases several days. An empirical method for determining time for initial set is to place a number of printed sheets between plain sheets of paper and subject them to pressure after

various periods of time. The setting time is noted as the period required to avoid any transference of the ink to the sheet above it.

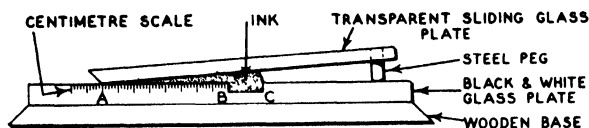


Fig. 8.—THE CRYPTOMETER.

OPACITY.

It is often necessary to determine the opacity of inks required for printing on coloured backgrounds, tin plate, etc. Opacity determinations can be accurately determined by complicated optical methods, but those based on the obliteration of contrasting backgrounds are the most convenient for ordinary works laboratory practice.

The simplest method of determining the opacity is to take a weighed piece of tin with a draught-board like surface in black and white and print successive layers of ink over this until the background is no longer apparent (Fig. 7). The opacity of the ink can then be determined by weighing the ink film applied and expressing the result in square centimetres covered per gram of ink.

The Pfund Cryptometer.

The Pfund cryptometer is a more easily handled method of determining opacity. The instrument consists of an optically plane piece of glass half of which is black and the other half opaque white, the black side being for light-coloured inks and vice versa. At the black and white join is a shallow depression into which a small quantity of the ink is placed. On the top of the glass slab fits another optically plane glass plate fitted at one end with two steel pegs projecting about 0.5 mm. The effect of sliding this top plate of glass across the lower one is to flow a film of ink of gradually increasing thickness across the lower glass. At some point during this increase of thickness the edge of the hollow depression containing the ink becomes invis-

ble owing to the opacity of the ink film on the glass plate being equal to the opacity of the thick film in the depression itself. The

position of the top plate when this arises is measured on a scale etched on the plate. The opacities of two inks will be inversely proportional to these scale readings. It is necessary to keep constant illumination of the instrument from the left-hand side and to take an average of a large number of readings moving the plate both forwards and backwards.

It is best to dilute heavy-bodied inks to a flowing consistency by mixing with a known volume of linseed oil. In such a case the opacity of the ink must be calculated from the scale reading for the mixture, having regard to the volume dilution effected by the linseed oil. The scale readings can be reduced to absolute values for the opacity of the ink itself if the steel peg projection is measured by means of a micrometer and the density of the ink and total effective length of the top glass plate is known. The opacity of the actual pigments used can also be calculated if the volume of pigment per unit volume of ink is ascertainable. The results obtained by such means as the above are only comparative and only strictly applicable to wet films. The opacity of inks sometimes changes considerably on drying owing to flocculation of the pigment.

SPECIFIC GRAVITY.

Owing to the presence of air pockets, a high viscosity and water repulsion, it is difficult to measure the specific gravity of printing inks directly by any of the standard methods. The following method based on the observation that there are no volume changes when inks are reduced with pure linseed oil is

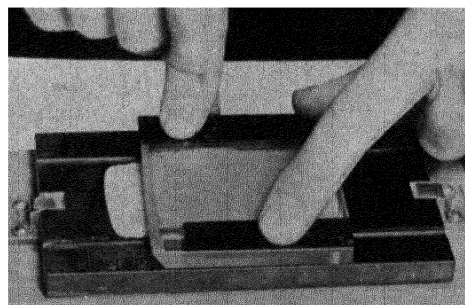


Fig. 9—USING THE PFUND CRYPTOMETER FOR LIGHT COLOURED INKS.

found to give reliable results. About 20 gm. of ink is accurately weighed into a 3-4-in. evaporating basin. A burette is filled with pure refined linseed oil and this is gradually run into the ink, keeping the mass homogeneous by continuously mixing by means of a glass pestle. The dilution is carried on until the mixture is of similar consistency to that of a thin enamel paint. The volume of linseed oil used is noted, and the evaporating basin is then placed in a vacuum desiccator which is evacuated until all the air is removed from the ink mixture. The gravity of this mixture is then taken by means of a 10 c.c. specific gravity bottle having a rather wider neck than usual. Great care has to be taken to avoid getting air bubbles into the gravity bottle, as the mixtures, especially if containing carbon black, are sometimes thixotropic, which renders the removal of air bubbles very difficult. It is best to place the filled specific gravity bottle in a thermostat for an hour to obtain even temperature throughout. The water content of the bottle must, of course, be determined at the same temperature.

It is necessary also to determine the specific gravity of the linseed oil at the same temperature. The specific gravity of the ink can be calculated from the following formula:—

$$\text{Sp. gr.} = \frac{Wd}{W + m - dV}$$

W = Weight of ink taken.

d = Specific gravity of mixture.

m = Weight of oil added (volume of oil $\times$ density).

V = Volume of oil added.

SEPARATION OF PIGMENT AND VARNISH.

The method of extraction in instruments of the Soxhlet type is not generally applicable to printing inks, owing to the extremely fine state of dispersion of the pigment, which renders it in most cases liable to come through the extraction

thimble. The most successful method of separating the pigment and varnish is by centrifuging, but even this is not successful with inks containing carbon black as the main pigment.

Ether or petroleum ether are the best solvents for the centrifuging method, but examination must be made to ensure that no fraction of the varnish, etc., is insoluble or precipitated by the solvents. The ink is first dispersed in the solvent in the cold, and the mixture subsequently refluxed. The preliminary dispersion is necessary as the plasticity of most inks makes dispersion by heat alone impossible. The dispersion is then transferred to a power centrifuge, which is rotated at a medium speed for such time as is necessary to effect separation of the pigment. The clear solution is poured off as completely as possible and the pigment redispersed in solvent and again centrifuged. This treatment is generally sufficient for ordinary work, but if a more complete separation is necessary, a further dispersion and centrifuging of the pigment may be necessary. The pigment is then dried to constant weight in an oven not more than 100° C. The solutions are combined, the solvent distilled off on a water bath, the last traces being taken off in vacuo. The residue is the main (non-volatile) portion of the medium. If volatile materials are present in the ink, these must be determined separately by steam distillation, and allowed for if the separation described above is being done quantitatively. Oil soluble dyes will of course appear in the varnish and must be allowed for in reporting on the pigment.

It appears that some selective absorption of the medium by the pigment takes place, as the physical properties of the medium extracted from an ink are invariably dissimilar to those of the materials used in its manufacture.

The analysis of printing inks is a matter of difficulty and often the results obtained do not justify the labour expended.

THE CONTROL OF SULPHURIC ACID MANUFACTURING PROCESSES

By W. H. IBBOTSON

MUCH might be written to cover the whole of the points involved in control of the processes of manufacturing sulphuric acid. In a work of this nature, therefore, it must suffice to describe briefly the general outlines before passing on to the tests involved in controlling the actual manufacture from the materials already dealt with.

Both processes, chamber and contact, involve the treatment of a burner gas containing as active participants in the reaction sulphur dioxide and oxygen. These gases in effect are combined, together with water, to produce sulphuric acid, though, as will have been gathered from previous articles describing the processes, the combination is not effected so simply as this statement might imply, nor is the means adopted identical in the two processes. It can, however, be deduced from these remarks that the principal tests required in control involve testing of gases from their source at the burner to the point at which conversion and combination with water has been achieved. After this point, and in the chamber process at intermediate stages also, the testing is that of liquid products.

The Chamber Process.

This process, employing nitrogen oxides as the medium for oxidation of the sulphur dioxide, calls for tests of burner gases, acid flowing to and from the Glover and Gay-Lussac towers, acid produced in the chambers, and exit gases. Additionally, temperature readings in the chambers themselves must be frequently observed to obtain indications of the progress of the reaction, as variations in the gaseous contents of the chambers affect the progress of the reaction and show themselves by consequent changes in temperature.

The Contact Process.

In this case, examination of burner gases, purified gases entering the converter, gases leaving the converter, acid used in scrubbers and absorbers, and temperature observations, furnish the necessary information for control. (See page 69.)

Burner Gases.

From remarks previously made with reference to the composition of the various materials used to produce sulphur dioxide it will be evident that the gases can and do vary somewhat. For instance, a pure gas such as is desirable for the contact process or for the production of high-grade chamber acid is best obtained by the use of a pure type of brimstone. The gases from pyrites containing notable impurities, or those from spent oxide—a particularly uncertain material—are more adapted to the production of commercial chamber acid.

Composition of Gases.

Gases from the combustion of brimstone consist of sulphur dioxide, oxygen and nitrogen, apart from small amounts of carbon dioxide and rarer gases from the atmosphere. Pyrites gases are similar in constitution, but in the case of gases from spent oxide some notable content of carbon dioxide and water vapour is found. This is due to the presence of woody and tarry matter, which as has been noted earlier, appears in spent oxide, and often the carbon dioxide amounts to as much as two per cent. Furthermore, gases from pyrites and spent oxide usually contain a little SO_3 . Gases from blende, which must have muffle heat in addition to its own heat of combustion to remove the sulphur content, are usually comparatively poor in sulphur dioxide and in some cases contain a fair amount of CO_2 . It should be remembered that the purpose of the roasting of such material is to obtain metal-

lurgical results, the acid product being only incidental.

Sulphur Dioxide Content.

The amount of sulphur dioxide thought desirable varies of course in different plants, but there is an upper limit due to the fact that it has been found necessary to maintain an excess of oxygen throughout the system to obtain satisfactory working. Actually oxygen is usually kept to such excess as will ensure a minimum of 5 per cent. oxygen in the exit gases. The constituent gases are estimated as per cent. by volume.

SO₂ Recorders.

The easiest way of ensuring complete observation of the quality of the burner gases passing to the plant is to install and use a recorder which automatically analyses and records the percentage of SO₂. It will readily be seen that if the SO₂ content is not allowed to exceed the given percentage accepted as suitable for the plant, say 8 per cent. as a case where brimstone is being used, the oxygen content must necessarily be in satisfactory proportion. Thus analysis of samples of gas at intervals which cannot possibly be so frequent is saved, provided other factors in the process are normal, and ordinary satisfactory working is proceeding. At the same time it provides a rapid control at the service of the burner operator.

Several types are in use, but all automatically take samples of the gas from a constant stream, which is pumped through the apparatus. The measured sample is forced into contact with a solution of iodine or caustic potash, the former being used where CO₂ is present and where it is desired to estimate actual SO₂ only, and the latter where no CO₂ is present beyond that from the atmosphere or where it is accepted as more or less constant or proportional. Actually, if CO₂ be present and excluded from estimation, the value of the SO₂ estimation as an indication of oxygen content is lost. Therefore it is best to employ caustic potash of 1.28 S.G. After removal of the SO₂ from the sample of gas, the unabsorbed gas is permitted by the automatic action to operate a pen-gear, which indicates the percentage SO₂ on a chart.

Analysis by Orsat Apparatus.

This apparatus consists materially of a

water-jacketed burette graduated to 100 c.c. and two or more double absorption pipettes packed with glass tubes to give contact surface and containing solutions which absorb the constituent gases, and a water-filled level-bottle and connecting tube. Sufficient heavy paraffin is floated on the surface of the water in the burette to prevent solution of gas in the water. The entrances to the burette and absorbers are controlled by stop-cocks, through which, when opened, the gas can be driven or withdrawn by use of the level-bottle. From the top of the gas burette to the gas inlet a glass tube passes and each absorber is connected. Entrance of the gas sample is governed by a three-way tap, giving communication from the burette to either the source of gas or atmosphere, or a third alternative, the closed position.

Absorbents Used.

The first absorption pipette is charged with caustic potash of 1.28 S.G. to absorb either SO₂ or both SO₂ and CO₂. If it is desired to differentiate between SO₂ and CO₂, iodine solution prepared from iodine and potassium iodide may be used and a second pipette is charged with caustic potash solution. A further pipette contains alkaline pyrogallol, prepared by dissolving one ounce of pyrogallol acid in 200 c.c. of the caustic potash solution, to absorb oxygen. This latter, when not in use, should be cut off from air to preserve the solution.

Operation.

Take a case where two pipettes containing caustic potash and pyrogallol are used. The apparatus is connected to the flue conducting the burner gas, and by alternatively raising and lowering the level-bottle whilst operating the three-way tap, several charges are drawn into the burette and discharged to atmosphere until it is certain that a true sample is being secured. Then a final charge is admitted and the level-bottle adjusted so that the water level in the burette coincides with the lowest graduation. The three-way tap is then put in the closed position and the sample is ready for analysis. The stop-cock of the first pipette containing caustic potash is opened, and by alternate raising and lowering of the level-bottle the sample is forced in and out several

times, until it can be safely assumed that the soluble gas has been absorbed, then it is slowly returned to the burette until the level of solution in the pipette reaches the mark, when the stop-cock is closed. The level-bottle is adjusted until the water level coincides with that in the burette and the percentage absorbed read off by reading the diminution in volume in c.c. in the burette. Similarly, the gas is passed into the second absorber containing pyrogallol and the remaining volume again read off. The oxygen percentage is found by deducting the first reading of SO_2 absorbed from the total percentage absorbed after the final reading.

Another Method of Estimating SO_2 .

The Orsat apparatus, whilst being useful for rapid estimations, does not lend itself for accurate use for SO_2 at later parts of the process. The following method is accurate and is applicable to estimations of SO_2 from the beginning to the end of the chamber process and for the gases entering and leaving the converter as well as burner gases in the contact process.

Known as the Reich test, it is based on the reaction between iodine and sulphur dioxide in the presence of water, producing hydriodic and sulphuric acids, and the fact that in the presence of free iodine, starch solution gives a blue coloration. A decinormal solution of iodine is used when dealing with burner gases.

Iodine and Starch Solutions.

Iodine solution is prepared by weighing out 12.692 gm. of pure resublimed iodine and adding this to a solution of about 17 gm. of potassium iodide in 200 c.c. of water in a litre graduated flask. The flask is agitated until all the iodine is dissolved, when the solution can be made up to one litre. It is advisable to check the solution against decinormal sodium arsenite solution to ascertain if it is actually decinormal. If correct, 1 c.c. of iodine solution is equivalent to 0.003207 gm. SO_2 , or 1.095 c.c. at 0°C . and 760 mm. pressure.

The starch solution is prepared by boiling soluble starch in water and should be freshly prepared. Paste is not suitable.

The Test Applied to Burner Gas.

A Drechsel bottle is charged with 10 c.c. of the decinormal iodine, 50 c.c. of dis-

tilled water, a little sodium bicarbonate and a few drops of starch solution. The outlet of the absorption bottle is connected with an aspirator bottle filled with water and the inlet with the gas source, a filter tube packed with glass wool being interposed where SO_2 is suspected or known to be present.

Water is run slowly from the aspirator into a graduated measuring jar, gas being by this means drawn through the absorbing bottle, which is kept agitated to ensure thorough mixing of the contents. The speed of flow should be such as to keep a continuous stream of small bubbles of gas passing into the iodine solution. When the colour deepens and then begins to fade, water is run off with extreme care, until the point is reached at which complete discharge of colour occurs. The flow is immediately stopped and the volume of water read off in the cylinder. This volume is equal to the volume of gas passed into the aspirator.

Calculation of SO_2 .

The volume of unabsorbed gas is corrected to 0°C . and 760 mm. The 10 c.c. of iodine solution used being capable of absorbing 10.95 c.c. of SO_2 , the volume of gas admitted will be equal to the volume unabsorbed plus 10.95 c.c.

Therefore, the percentage

$$\text{SO}_2 = \frac{10.95 \times 100}{10.95 + \text{vol. unabsorbed.}}$$

Example: Corrected volume of unabsorbed gas = 110.3 c.c.

Then volume of gas admitted = 110.3 + 10.95 c.c.

$$\text{SO}_2 = \frac{10.95 \times 100}{10.95 + 110.3} = \frac{1095}{121.25} = 9.03\%.$$

Modifications of the Test.

If it be desired to estimate SO_2 at a later point in the chamber process where nitrogen oxides are present in the gas, it is necessary to guard against interference with the reaction. To this end therefore, 10 c.c. of a saturated solution of sodium acetate is placed in the absorbing bottle in addition to iodine, water and starch, omitting sodium bicarbonate. The SO_2 is calculated in the same way, and the nitrous content may additionally be approximated by titrating the contents of the absorption bottle with decinormal caustic soda, with phenolphthalein as indicator, and deducting 20 c.c. from the

decinormal soda used. The deduction is necessary to allow for hydriodic and sulphuric acid formed. The remainder of the soda used will be that required to neutralise the nitrogen oxides which may be calculated as nitrous or nitric acid.

A further modification is advisable when testing exit gases or gases at the rear of the chamber system. In these instances the iodine solution should be diluted to 1/250 or even 1/500 normal, and 10 c.c. of this weaker solution used in place of decinormal, the difference being, of course, allowed for in the calculation.

Testing for Oxygen at Later Points in System.

If it be desired to estimate oxygen in gases leaving the chamber system for the Gay-Lussac tower, the Orsat apparatus will be found suitable. The gas sample should, however, be first passed into the caustic potash pipette and a reading taken before being passed into the pyrogallol. The difference between the two readings will again indicate oxygen percentage.

Testing Converter Gases in Contact Process.

To keep observation on the working of converters it is necessary to make tests frequently on the gases entering and leaving. In this way the standard of conversion attained may be checked and adjustments made if necessary. For this purpose the simplest method lies in the use of the Reich test at the inlet and outlet. It is not sufficient however to make a simple comparison of the percentage SO_2 at the two points—the fact that SO_2 has been converted to SO_3 between the two points with consequent diminution in volume, must be allowed for in the calculation. This is done by using the formula

$$C = \frac{100(a - b)}{a(1 - 0.015b)}$$

a being percentage SO_2 at inlet, b percentage SO_2 at outlet, and C percentage conversion.

Exit Gases.

In accordance with the Alkali Act, 1906, the exit gas from the chamber process must not exceed in total acidity the equivalent of 4 grains SO_3 per cubic foot. It is, therefore, necessary to check the exit gases at intervals to ensure compliance and to avoid unobserved loss of a valuable product. The official method now used

involves the use of a collapsible rubber aspirator or bellows, which when extended contains one-tenth of one cubic foot. This aspirator is charged with about 200 c.c. of distilled water, to which 4 or 5 c.c. of neutral hydrogen peroxide (20 vols) has been added. Charging is accomplished by closing the aspirator, placing the thumb on the discharge hole in the mouthpiece, and syphoning the peroxide solution through the rubber sampling tube attached to the nozzle by lowering the aspirator.

The rubber sampling tube is then attached to a glass tube, which is inserted through a bung into the exit stack, the aspirator in the closed position and a plug in the outlet hole in the nozzle. A full charge is then drawn by extending the aspirator, pinching the rubber inlet tube at the conclusion of the extension. The inlet tube is next sealed close to the nozzle by a spring clip and agitation of the aspirator is continued at frequent intervals for a period of twenty minutes. This is necessitated by the fact that the nitrous contents of the gases are not accounted for unless this time is taken—theirs is a time reaction, unlike that of the sulphur dioxide with peroxide.

At the end of this period the aspirator is discharged into a glass bottle, a drop of methyl orange added, and titration with a five-sixths normal caustic soda solution proceeded with until neutrality is attained. The number of c.c. soda used, multiplied by five, equals acidity in grains in terms of SO_3 .

Other Uses of the Aspirator.

A similar test, employing the same solution of peroxide, may be applied to the exits from contact plants, scrubber gases from concentration plants, and also their fire-gas chimneys. In these cases, no time reaction need be allowed for, so it is the usual practice to aspirate half of one cubic foot of gas, that is, five aspirations. The outlet hole of the aspirator is not plugged in this case, but is sealed with the thumb whilst aspirating. After each charge the rubber inlet tube is sealed by being turned over the nozzle with a finger, the gas charge and liquid contents agitated for a minute, the treated gas being then expelled through the outlet, keeping the inlet tube still sealed whilst so doing. The operation is repeated five times, then the acidity is titrated as previously

described. In this case direct reading of the c.c. soda used gives grains SO_3 per cubic foot of gas. The permissible limit for concentration exits and chimneys is 1.5 grains.

Acid in Circulation in the Chamber Process.

Efficient working of chamber plant is not governed by gases alone, but also by acid flowing down the Glover and Gay-Lussac towers, respectively supplying and recovering nitrogen oxides. It is obvious then that some estimation of their nitrogen content is necessary. It is also necessary on occasion that the weak or chamber acid be examined for nitrogen content, as "nitre" is sometimes carried down. Strength also must be determined to ensure efficient absorption in the Glover tower.

The nitrometer, which has been referred to in dealing with nitrate of soda, is the most convenient means for estimating "nitre" in all these acids.

Testing for "Nitre" Content.

In the case of acid passing from the Gay-Lussac to feed the Glover, acid passing down the Glover, or any other acid in which comparatively large amounts of "nitre" may be expected, 1 c.c. is introduced into the cup of the nitrometer and admitted through the stop-cock, which is so manipulated as not to admit any air. The cup is then washed with 1 c.c. of water, which is likewise admitted. The graduated limb is then agitated until evolution of gas has ceased, when, after levelling—as previously described—the volume of NO evolved may be read off. The reading, owing to the increased temperature following the reaction will not, of course, be accurate, but it is quite satisfactory for control purposes, and conditions being always practically the same, it is comparative.

In this country it is usual to work out "nitre" contents on a volumetric basis, as ounces of nitrate of soda per cubic foot of acid, disregarding gravity. Now 1 c.c. of NO at N.T.P. is equivalent to 0.0037963 gm. of nitrate of soda. Thus each c.c. of NO represents this weight of nitrate per c.c. of nitrous vitriol, or converted to the accepted basis, 3.79 ounces per cubic foot. For works purposes it is convenient to make out a table from 0.0 c.c. NO in

fractions of 0.1 to, say, 20.0 c.c., from which values may easily be read.

Strength of Chamber Acid and Acid in Circulation.

For works purposes, and indeed for sale purposes in many instances, strength of sulphuric acid is determined by hydrometer, using the Twaddell scale. This scale is based on specific gravity, zero being equivalent to 1.000 S.G. at 60° F. and each degree equivalent to 0.005 S.G. increase over 1.000. Thus, to take works figures, 140 Tw. = 1.700 S.G. and 100 Tw. = 1.500 S.G. Whilst not exactly true over all the range of strengths of sulphuric acid, a correction of 1 Tw. is made for a variation of 10° F. in the temperature of plant acids. Thus a temperature of 80° F., at which a given strength acid will be less dense than at 60° F., necessitates a correction of plus 2° Tw. Likewise, at 40° F. a deduction of 2° Tw. from the degrees as read will be required to obtain °Tw. at 60° F.

The Twaddell hydrometer is applied in this way to check strengths of all circulation acids and acid condensing in chambers and falling in the "drips" fitted thereon.

Estimation of H_2SO_4 .

The most convenient method of weighing the acid is found in the Lunge-Rey pipette. This apparatus permits a small quantity to be drawn into the inner part by the following series of operations. The lower tap is closed, the upper one opened and suction applied at the top. Whilst still under suction, the upper tap is closed, the tip immersed in the acid sample and the lower tap opened. This admits a portion of acid into the pipette. After rinsing round, the acid is discharged and the operations are repeated to obtain a portion in the pipette which will be the actual acid tested.

Next, the outer tube is replaced over the tip and the whole apparatus weighed. A portion of the acid, say two or three gm., is then run directly into about 100 c.c. of water, and the complete apparatus reweighed. Thus the actual weight of acid used is obtained. The well-mixed acid solution is then titrated with the soda, using methyl orange or red as indicator.

Testing "Oleum."

Acid of this type, produced by the contact process, cannot be tested on

precisely the same basis as it contains SO_3 and usually some SO_2 in addition to H_2SO_4 . Whilst simple titration and calculation may be found satisfactory for some works purposes, in other instances, such as sale acid, it is desirable to make some differentiation between acidity due to H_2SO_4 , SO_3 and SO_2 . Then the following method is employed.

A weighed portion is taken in a similar manner to that adopted for ordinary sulphuric acid, the weighed acid being run into water and the solution being made up to 500 c.c. and well mixed.

First 100 c.c. of the acid solution is titrated with standardised decinormal iodine to estimate SO_2 , each c.c. of iodine used being equal to 0.003203 gm. SO_2 . A further 100 c.c. is titrated with normal alkali (or half normal if more accuracy is desired) with methyl orange as indicator, and from the result of this titration must be deducted the acidity due to SO_2 .

When SO_2 is titrated by alkali with methyl orange the end-point is reached when the first atom of hydrogen has been neutralised. Thus one equivalent of SO_2 in this case represents two of iodine. So instead of deducting 0.1 c.c. of normal alkali for each c.c. of decinormal iodine used in the SO_2 titration to obtain the alkali equivalent for SO_3 and H_2SO_4 , 0.05 c.c. alkali for each c.c. of iodine is deducted. The remaining normal alkali can be calculated as with ordinary acid to H_2SO_4 if this is satisfactory for the purpose. Here the excess of the result over 100 per cent. may be assumed to be H_2O equivalent to make H_2SO_4 with the SO_3 present.

Where it is desired to obtain the various acid constituents separately this can be done from the titrations carried out in the following manner. First the total SO_3 is found by multiplying the c.c. of normal alkali neutralised by H_2SO_4 and SO_3 (that is, total alkali less the appropriate allowance for SO_2 mentioned above) by 0.040035. To this is added the SO_2 found by iodine titration and the sum deducted from the weight taken. Assuming this to be water, the equivalent SO_3 to make up to H_2SO_4 is calculated by $\text{H}_2\text{O} \times 4.443$. This calculated SO_3 being then deducted from the total SO_3 previously found will give the actual SO_3 .

Testing Burned Residues.

Whilst the burning of sulphurous

materials results in conversion of most of the sulphur into sulphur dioxide, some small proportion remains in the residues, and under adverse conditions, this may be large enough in quantity to entail considerable loss. It will, therefore, be evident that the testing of residues is of some importance as a check on the efficiency of combustion in the burners. Some proportion of the sulphur remaining is retained in the "fixed" form, that is, not recoverable by burning. This loss is, of course, inevitable, but such sulphur as is present as elemental sulphur or combustible sulphides is, within limits, an avoidable loss. The test, therefore, which is of value to the acid manufacturer is a combustion test which indicates what avoidable loss of sulphur is occurring in the burners.

Carrying Out the Test.

The residues are carefully sampled to obtain a portion representative of say, one whole day's run, dried if the discharged material has been slaked, and ground to a fine powder. Of this fine well-mixed powder 0.5 gm. is weighed out into a weighed porcelain combustion boat. This is then inserted into the combustion tube which is plugged at each end with a hard rubber bung through which a $\frac{1}{4}$ -in. glass tube passes. One end is attached to an oxygen cylinder and the other to the series of absorption tubes which should be at least two in number. Heat is applied to the combustion tube and oxygen allowed to pass at such a rate as will maintain a steady stream of bubbles in the absorption tubes. Heating is continued until fumes have ceased to leave the combustion tube for some minutes. The tube is then allowed to cool off for about 10 minutes, oxygen meanwhile being passed. The contents of the absorption tubes are then emptied into a flask together with washings and the combustion tube, after careful removal of the boat, is also washed into the flask. The contents of the flask are then titrated with standard soda solution, using methyl orange or red as indicator.

Testing Acid Ready for Sale.

Testing for H_2SO_4 content of the higher strength acids, 96 to 100 per cent. and "oleum" has already been described. The usual products of the chamber process, B.O.V. (77 per cent. acid produced at the

Glover tower or by chamber acid concentration) and D.O.V. or R.O.V. (94 to 96 per cent. acid produced by concentration) may be similarly tested by alkali titration if circumstances call for it, but the usual practice is to use the Twaddell hydrometer and to compare the reading at 60° F. with the tables which appear in many published works. Actually it is more usual to buy and sell acid up to 94 per cent. on a basis of degrees Twaddell rather than on percentage.

Impurities in Commercial Acid.

In commercial acids some little latitude is permissible with regard to impurities—pure acid for analytical purposes and acid to conform to B.P. standards must be specially prepared. The common impurities to be looked for are nitrogen acids, iron, lead and arsenic. The first-named can be estimated, if present in marked quantity, by use of the nitrometer, as already described, but in this instance 5 or 10 c.c. is charged. Very small amounts can be detected by the use of diphenylamine, a little of which should be dissolved in strong pure sulphuric acid, a few c.c. of this solution being then carefully added to a little of the acid to be tested in a test-tube, so that mixing is only gradual. A distinct blue colour will develop at the point of contact of the layers and spread through the mixed acids if nitrogen acids are present.

Estimation of Iron.

Iron usually appears in commercial acid made from pyrites or spent oxide. It is most conveniently estimated by weighing out about 25 c.c. of acid in a weighing bottle, washing this into a beaker with about 150 c.c. of distilled water, and boiling the mixture to obtain complete solution of any solid sulphate. After cooling somewhat, a little pure granulated zinc is introduced, so that evolution of nascent hydrogen may reduce any ferric salt to the ferrous state. The contents of the beaker are then washed into a 250 c.c. graduated flask, stoppered, rapidly cooled in a stream of water and the volume is made up to the mark with distilled water. The whole after mixing is then filtered through a filter paper in which a little zinc has been placed, and 200 c.c. of the filtrate is immediately titrated with decinormal potassium permanganate solution, which

has been standardised against pure iron, until a slight permanent pink coloration is observed. The amount of iron thus found will be that contained in four-fifths of the weight of acid taken. From this the percentage of total iron will be readily calculated.

Testing for Lead and Arsenic.

Lead is usually estimated by precipitating as sulphate. This is done by diluting a measured quantity of the acid, 50 or 100 c.c., with an equal bulk of water and twice the bulk of alcohol, shaking and standing overnight. The lead present will appear as sulphate and is collected by filtration, washed on the paper with alcohol, dried and ignited in a porcelain crucible. To avoid reduction, it is advisable to burn the paper, prior to ignition in a dull-red muffle, in a coil of platinum wire over the crucible. The weight of sulphate $\times 0.6831 = \text{Pb}$. It should be noted that this test is usually only applied to high strength concentrated acid. Obviously, any solid matter, such as might be present in dirty samples of Glover acid, would seriously vitiate the accuracy of the test.

Arsenic, a common impurity, particularly in acid made from pyrites, can be detected by a simple Marsh test, and if any considerable quantity be present, estimated by the following method:—

A measured volume, say 25 c.c., of the acid is diluted with about 100 c.c. of distilled water in a conical flask and SO_2 is passed until the acid solution is saturated and smells strongly of the gas. The excess SO_2 is expelled by boiling, whilst at the same time, CO_2 is passed. After boiling off all SO_2 , sodium carbonate is added in small quantities until the acid is almost neutralised, when neutralisation is completed by addition of sodium bicarbonate. Two or three gm. more in excess are added and the mixture is immediately titrated with standardised N/100 iodine solution, using starch indicator, until a blue coloration persists. Each c.c. of the iodine indicates 0.0004948 gm. As_2O_3 and the percentage arsenic in terms of As_2O_3 can be calculated, the weight of acid taken being deduced from volume and gravity.

Small quantities of arsenic are best estimated by the modified Gutzeit method, as described elsewhere (p. 442).

THE ANODIC OXIDATION OF ALUMINIUM

By S. WERNICK, Ph.D., M.Sc.

ELECTRODEPOSITION processes thus far described, e.g., nickel and chromium plating, are largely concerned with electrochemical phenomena which take place at the *cathode*. In recent years, however, a number of highly important industrial applications have been developed which centre round electrolytic phenomena which occur in the neighbourhood of the *anode*. Such processes are termed anodic processes. Two of the most important industrial examples are the electrodeposition of rubber, which takes place at the anode, and the anodic oxidation of aluminium. It is proposed to deal briefly with the latter process in the present article.

The commercial application of aluminium has greatly extended during the present century. Actually, more than 30 times as much aluminium is used to-day as in 1900. The metal possesses important properties which make it very useful to the engineering, building, architectural, and a host of allied industries. It is very light, being only one-third the weight of the common metals—iron, copper, brass, etc., and when alloyed with other metals, it produces alloys of remarkable strength and toughness.

Corrodibility.

The one great drawback of aluminium is its relative corrodibility. If a piece of aluminium is left exposed to the atmosphere without any protective covering, it soon forms a white, powdery substance on the surface. This is a corrosion product which is equivalent to the forma-

tion of rust on unprotected iron or steel, and if the corroding conditions are marked, e.g., in marine atmospheres, this corrosion may in time "eat" completely through the aluminium.

A freshly exposed aluminium surface is actually much more corrodible than one which has been left exposed to the air, since very fortunately a very thin invisible film of aluminium oxide forms immediately on the surface which confers a considerable degree of protection. Were this not the case, it would be impossible to use aluminium at all for most purposes, since it would rapidly corrode away. The fact that the very thin oxide film formed naturally by the action of the atmosphere is highly protective has been known for a long time and it led to the idea that if this oxide film could be made thicker by some artificial means, then the protection conferred might be greatly increased. This possibility has been completely realised and has resulted in the perfection of electrolytic processes for producing the oxide film, which are now known as anodic, or anodising, processes for treating aluminium.

The manner in which this is effected is as follows. A suitable electrolyte is used, the most important constituent of which usually comprises an acid. The aluminium

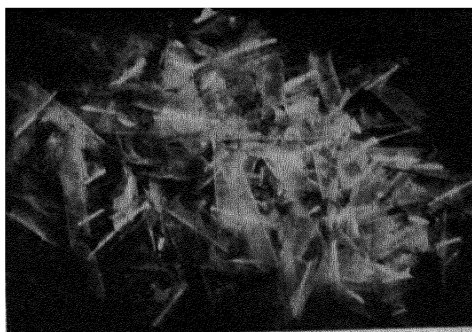


Fig. 1.—ANODIC FILM (LARGELY ALUMINIUM OXIDE) DETACHED FROM ALUMINIUM BY A SPECIAL METHOD APPLIED BY THE AUTHOR.

article to be anodically treated or "anodised" is then attached to the positive, or anode, side of the electrolytic circuit, immersed in the solution and the current switched on. The cathode side of the circuit usually consists of some inert or relatively non-reactive material, e.g., lead or iron, or

even aluminium. The result of the passage of current is to produce the constituents of water, hydrogen and oxygen respectively, at the cathode and anode. The oxygen at the anode, which consists of the aluminium article, attacks the metal superficially to form aluminium oxide. This film of oxide thickens as the passage of the current is continued. A thickness of the order of one-thousandth of an inch of oxide may be achieved if desired, this being many hundred times the thickness of the "natural" oxide film formed by contact with the atmosphere.

Typical Processes.

The various anodic processes which are in use vary very much with the nature of the electrolyte employed. One of the first processes established was a British process developed by two Government workers, Bengough and Stuart, who used a weak solution of chromic acid. The concentration of the latter is about three per cent., and, since the conductivity of such a weak electrolyte is necessarily low, comparatively high voltages (relative to those employed in electroplating practice) are used. The voltage is raised in steps as follows: In the first fifteen minutes, the voltage is raised to 40 volts and kept at this figure for 35 minutes; in the course of the next five minutes, it is raised to 50 volts and kept at this voltage for the final five minutes. The total time of processing amounts to one hour.

The temperature of the bath is kept at about 45° C., while the cathode material used may be carbon, or stainless steel, the latter having been found far more effective, if more expensive.

This process results in the production of a hard, highly resistant oxide coating which possesses an opaque, grey colour and, since it is integral with the base metal, it is tenaciously adherent to the surface. One of the drawbacks of the Bengough process, as this method of anodising has become known, is that it is a "batch" process, i.e., as the voltage is not constant throughout the process, it is necessary to load the bath with a batch of articles at the beginning of each treatment, after which it is not possible to add further articles until the completion of the voltage cycle. This disadvantage is overcome in other anodising processes which utilise sulphuric or oxalic acid as electrolytes.

These are more highly conducting solutions and enable the passage of adequate current at comparatively low, and also *constant* voltage. Sulphuric acid electrolytes, for example, are operated at a steady voltage of 10 to 20 volts, while the time required to produce a highly protective coating is also much reduced, some 20 to 30 minutes sufficing to effect this. This type of electrolyte is worked at room temperature, while the finish of the oxide coating differs from that produced by the Bengough process in that it is clear, translucent and silvery in appearance.

The tank material, which must be resistant to sulphuric acid, is usually lead, and this functions in a dual capacity, the negative terminal being attached to the tank, which then acts as the cathode of the electrolytic circuit.

Properties of the Oxide Film.

The corrosion resistance of the oxide coating has already been mentioned, and constitutes its most important property. The film is also extremely hard. This will be readily appreciated when it is realised that aluminium oxide, or alumina, of which the film is largely composed, is also the basic constituent of a number of semi-precious stones, such as the ruby and sapphire, the hardness of which is considerable. Its actual hardness lies between quartz and corundum, which are well known as standards of hardness. The practical effect of this is that the surface resists wear extremely well, so that it is entirely suitable as a finish which has to withstand constant rubbing or handling.

Adsorptive Property.

One of the most important properties of the oxide coating is its capacity of adsorbing (i.e., chemical absorption) of other substances. A freshly produced piece of anodised aluminium is capable of taking up dyes, stains, oils, waxes, etc., very much in the way that blotting-paper does. This is due to the very fine open structure of the surface of the film. The adsorptive capacity decreases with time and in a few days it practically disappears completely. As a result of this property, it is necessary to exercise extreme care in handling a metal surface which has just been anodised, since it will even absorb the grease and natural oils present on the fingers, which would result in finger-print impression on the surface.

THE MANUFACTURE OF MARGARINE

By M. D. CURWEN, B.Sc., A.I.C.

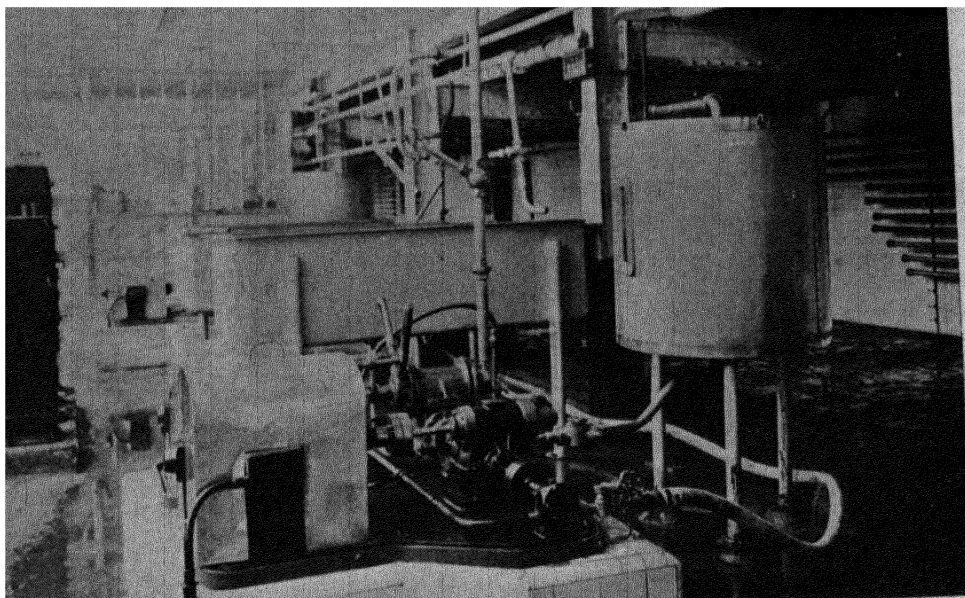


Fig. 1.—EMULSIFIER FOR CONTINUOUS PRODUCTION.

THE development of this important foodstuff is due to Mège-Mouries as a result of a competition, initiated by Napoleon III during the Franco-German War of 1870, for the production of a butter substitute.

Modern methods differ considerably from those then employed and the modern manufacturer has at his disposal not only a much greater variety of oils and fats, but also much more scientific means of attaining a valuable edible product.

Definition of Margarine.

Margarine may be considered to be a very stable emulsion of oil and water, actually a carefully chosen emulsion of animal and vegetable oils with milk, stabilised by the addition of special chemicals.

There are two classes of margarine :—

(1) Oleomargarines, in which the quantity of animal fats and oils predominate over the vegetable oils.

(2) Vegetable margarines, in which the quantity of vegetable oils predominate.

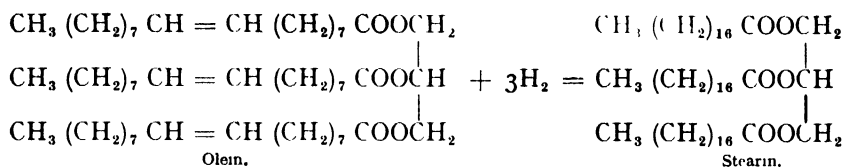
Types of Oils and Fats.

Single oils and fats are never used alone. The choice of the kind to be utilised depends on the desired final product (melting point and other characteristics) and the very important economic reason of price.

Of animal fats the most general in use are lard, premier jus (the oil obtained by rendering the fat of ox-heart and kidney), oleo oil, etc., while of vegetable oils there are palm, arachis (ground nut), coconut, cottonseed, soya bean, etc. Furthermore, recent years have seen the development of hydrogenation of vegetable oils. This process of the addition of atoms of hydrogen to the unsaturated portion of oils converts them to products of higher melting point. Thus, olein, which is liquid at ordinary temperatures and contains three unsaturated linkages, is converted to solid unsaturated stearin.



Fig. 2.—"MULTIPLEX" MARGARINE KNEADING MACHINE, SHOWING EXTRUSION END.



Thus, by suitably regulating the hydrogenation and consequently controlling the quantity of hydrogenation, the manufacturer can within limits obtain a fat of any desired melting point and a fat less liable to deterioration. The process consists in passing hydrogen through the oil (at elevated temperatures and pressure sometimes) in the presence of a catalyst, generally nickel.

Refining of Fats and Oils.

The raw materials, the oils and fats in solid and liquid form, must be freed before use from extraneous matter, free fatty acids and most of their colour. The first process is that of treatment with caustic soda, which eliminates acidity and part of the colour. The caustic soda solution (the quantity depending on the acidity of the oil and its colour) is mixed together in tanks fitted with stirrers and steam coils at a temperature of 30° C. to 50° C. After standing, the "foots" or "soap stock" separates out at the bottom and

is removed. Sodium carbonate may be used instead of caustic soda, but very little colour is removed by such means.

Excess soda is now washed out of the oil, which is then bleached by the addition of fuller's earth or activated carbon and heating to a temperature slightly over 100° C. The fuller's earth is then removed by filtration through filter-presses and the oil is then deodorised by means of steam distillation under high vacuum in autoclaves. This process not only removes odour but also the last traces of water and unsaponifiable matter. The autoclaves are lined with a special alloy or glass in order not to affect the edible qualities of the fats and oils.

Compounding of Oils.

The manufacturer, since his final product may possess a melting point between, say, 24°–32° C., has a fair latitude in choice from the wide range of materials at his disposal. The fats and oils arrive from the refinery and are charged into large

melting tanks, double jacketed for heating with steam or for cooling, and provided with stirring gear for mixing the different fats and oils during heating to obtain a homogeneous mixture. The mixed oil is then pumped to a series of jacketed pans for the next process of emulsification with milk.

Vitamins.

At this point it is convenient to mention that many modern factories are producing vitaminised margarines by incorporating with the compounded oils the requisite quantity of vitamin concentrate, usually obtained by extraction from cod or halibut liver oils. It is fair to remark that many such margarines are in consequence considered equal to the best summer butter in the vitamin A and D content.

Preparation of Milk.

The object of the addition of the milk is twofold: to give the desired flavour of butter to the margarine and to act as an emulsifying agent, the flavouring properties being brought out by treating the milk with lactic acid bacteria, which induce the required acidity and aroma.

New milk is first pasteurised so that all pathogenic germs are destroyed. The milk is then ready for inoculation and normally a mixture of pure cultures and not of a single culture is employed. Among those favoured are *B. lactic acid* *Leichmann*, *Streptococcus lacticus* and *B. bulgaricus*. Following inoculation the milk is placed in aluminium vessels and ripened at constant temperature until a definite acidity is reached. Large cement tanks filled with water at constant temperature is a common method in use.

Emulsification of Oils and Milk.

The mixing of oils and milk to form a stable emulsion may be carried out in batches or by a continuous process. The batch method entails a plant consisting merely of tanks, jacketed to allow of heating and cooling and provided with the necessary stirring gear to ensure rapid agitation. Usually the milk, after being strained, is charged into the mixing tanks first, is then agitated and the oils are added slowly in a stream or as a spray. It will be realised that, since the melting point of the mixed oils varies considerably, the temperature in the tank also

varies with the type of oils—from 5° C. to 35° C., so that no definite temperature can be laid down. During the mixing process, yellow harmless colouring materials and emulsifying agents are added. Milk alone will not produce a stable emulsion, so that small quantities of special emulsifying agents such as glucose, lecithin, albumen, etc., are added at this point.

The continuous process employs a special type of emulsifying machine such as that shown in Fig. 1. This type is electrically driven, the mixed oils from the storage tanks and the milk being fed through two separate pipes into a horizontal cylinder under pressure. This cylinder is jacketed for heating and is provided with a number of internal rotating blades. A high speed of rotation is maintained (about 1,000 r.p.m.) so that thorough and intimate mixing is made, and the mixture is ejected through a series of small holes. A plant as small as is seen in the photograph and driven by a 3-h.p. motor is capable of emulsifying 3 tons per hour.

Cooling the Emulsion.

The cream of margarine thus formed is then discharged down an inclined chute where it meets a stream of ice-cold water, this sudden drop of temperature stabilising the emulsion and forming tiny granules. This method of cooling is not, however, always adopted, for the final water content of margarine (with an upper limit of 16 per cent.) cannot easily be controlled.

A more modern method is to spray the emulsion on the juncture of two rotating drums placed very closely together and cooled internally with brine. The fine film is thus rapidly cooled and scraped off the drums as they rotate in the form of fine flakes. These are collected in large trucks, which are wheeled away to special store rooms, where maturing and ripening at constant temperature is reached. Perfect cohesion of the particles or crystals is then attained.

After maturing, the margarine undergoes a series of kneading treatments in wooden machines of various types such as the Multiplex rolling machine or the rotary kneader. Here the water content is reduced to the desired proportion—about 12 per cent. Finally, if salt is to be incorporated, this is carried out on kneading tables.

PETROLEUM AND ITS PRODUCTS

PART VII.—THE TESTING OF FUEL OILS AND LUBRICATING OILS

By F. N. HARRAP, M.Sc.

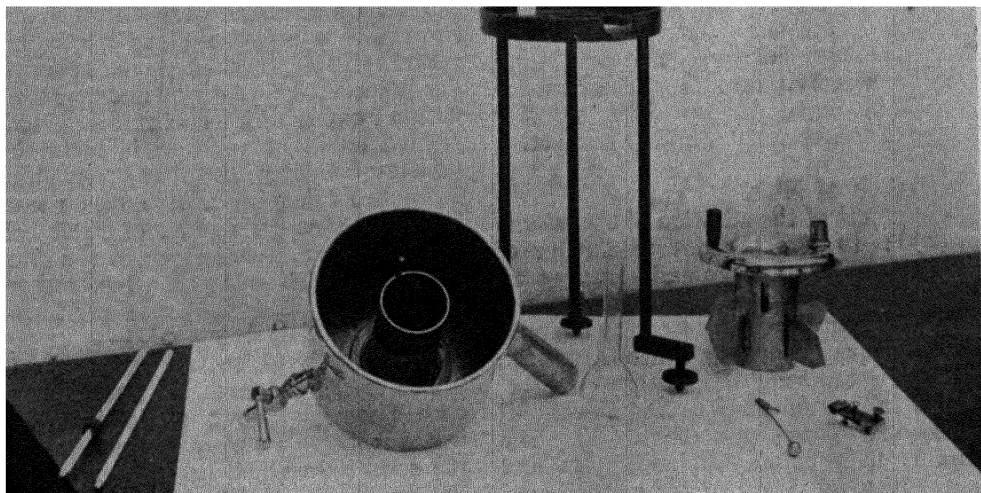


Fig. 1.—REDWOOD VISCOSITY (1).

The various parts of the apparatus are shown in this photograph. The oil cup and its heating bath are on the left, and the stirrer, silvered brass sphere and thermometer clip on the right.

Gas Oils and Fuel Oils.

THE following tests are normally made on samples of gas oil or fuel oil :—

- (1) Specific gravity ;
- (2) Flash point ;
- (3) Viscosity ;
- (4) Calorific value ;
- (5) Sulphur ;
- (6) Asphaltenes (hard asphalt content) ;
- (7) Water ;
- (8) Pour test (or cold test) ;
- (9) Ash ;
- (10) Carbon residue.

In the case of gas oil samples, which are usually distillates, determinations (6), (7) and (9) can, as a rule, be omitted. Special tests are available for checking up the distillation range of gas oil and for evaluating its gas-making properties, but these will not be discussed in the present

article. Finally, as the purchaser of gas oil may buy very largely on colour it is usual to determine this, although there is no generally accepted method.

Specific Gravity.

This is determined by means of a hydrometer (as described on page 85), although with viscous oils it is necessary to use a specific gravity bottle. The method is a well-known one, the specific gravity being obtained by ascertaining the ratio between the weights of oil and water when the bottle is filled respectively with the two.

Flash Point.

Since in all cases the flash point exceeds 150° F. the Abel instrument cannot be employed, and the test is carried out in the Pensky-Martens tester. The details of the

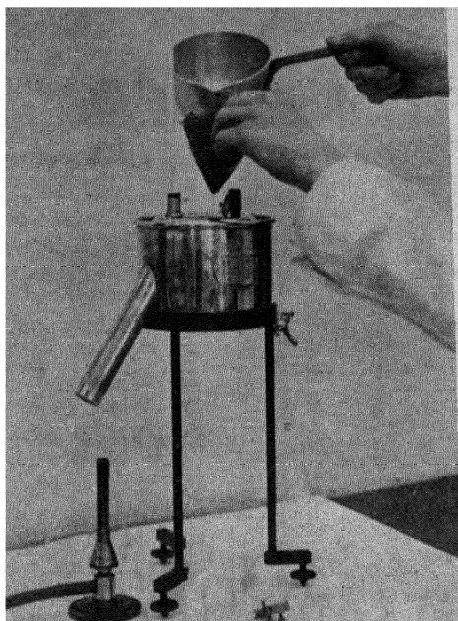


Fig. 2.—REDWOOD VISCOSITY (2).

The sample is filtered into the oil cup, up to a level indicated by the gauge in the oil cup.

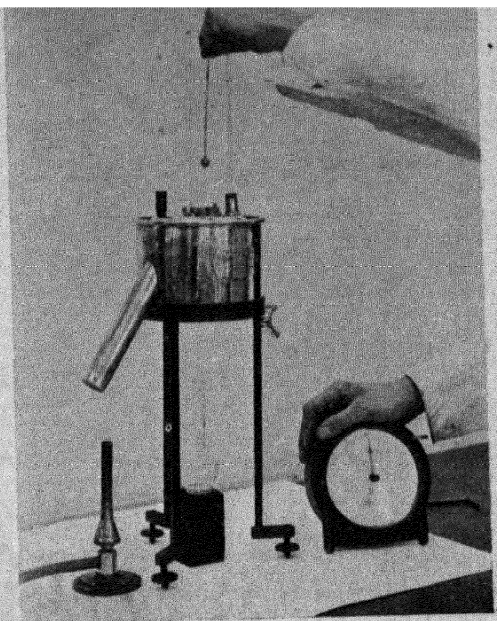


Fig. 3.—REDWOOD VISCOSITY (3).

When the temperature of the oil has been adjusted to the testing temperature, the brass sphere which closes the agate jet is raised and the stop-clock is started at the same time.

method have already been described, under the heading of "Kerosene" (page 948).

Viscosity.

Modern tendency is in favour of expressing the viscosity of petroleum products in scientific units (poises or stokes), but practically all the tests made in this country are still carried out in the Redwood viscometer, and for this reason only the Redwood viscosity method will be described.

The Redwood Viscometer.

The instrument consists of a silvered-brass oil-cylinder, provided with an agate jet of standard dimensions, and surrounded by a water bath (for temperatures over 200° F. oil are used as a heating medium). A copper side-tube provides a means of heating the bath liquid, which is stirred by means of a revolving agitator which forms part of the apparatus. The agitator carries a thermometer which indicates the temperature of the bath, whilst the temperature of the sample in the oil-cup is recorded by a second thermometer which

is carried in a clip fitting on a short standard attached to the oil-cylinder. Inside the oil-cylinder is a small bracket terminating in an upturned point, and indicating the height to which the sample is filled in the cup. The agate jet of the oil-cylinder is closed by means of a silvered-brass sphere attached to a wire, the brass sphere resting in a hemispherical cavity. The various parts of the apparatus are shown in Figs. 2 and 3.

The Redwood Method of Test.

The oil-cup must first be cleaned carefully, preferably with paper rather than with cloth, as with the latter there is a possibility of fibres being detached and lodging in the jet. The jet must be examined and, if necessary, cleaned by means of a piece of soft string. After levelling the apparatus the external heating bath is filled with water (or with a heavy mineral oil for tests at temperatures over 200° F.), so that the level coincides approximately with that of the oil in the inner cup. In all cases it is desirable to heat the liquid used to a temperature slightly higher than that at which it will

ultimately be maintained, before transference to the viscometer.

The sample to be tested is heated to a temperature slightly higher than the test temperature (normally 100°F. for fuel oils and 60°F. or 70°F. for gas oils), and is then filtered through fine copper gauze into the oil-cup (Fig. 2), to a level slightly above the top of the gauge in the cup. The thermometer is suspended vertically in the oil by means of the clip, so that it is approximately mid-way between the centre and the wall of the cup, with the bulb $\frac{1}{4}$ in. from the bottom of the cup. The temperature is adjusted to the test temperature and

when it has become constant the level of oil in the cup is adjusted to the correct height. The test is then commenced by lifting the small brass sphere closing the agate jet and suspending it in the oil-cup by means of the hook in the wire, this being hung on the side of the oil-cup during the test. When the brass sphere is raised from the agate jet a stop clock, or stop watch, is started and the oil is allowed to flow from the jet until exactly 50 c.c. is collected in the standard flask placed below the jet. When the meniscus of the oil passes the 50 c.c. mark on the neck of the flask the stop clock is stopped, and the number of seconds required for 50 c.c. flow of oil is obtained. This figure is recorded as the viscosity of the oil at the test temperature (e.g., 250 seconds Redwood 1 at 100°F.). It is necessary to describe the instrument as the Redwood 1 viscometer to differentiate it from the Redwood No. 2 instrument which is occasionally used for very

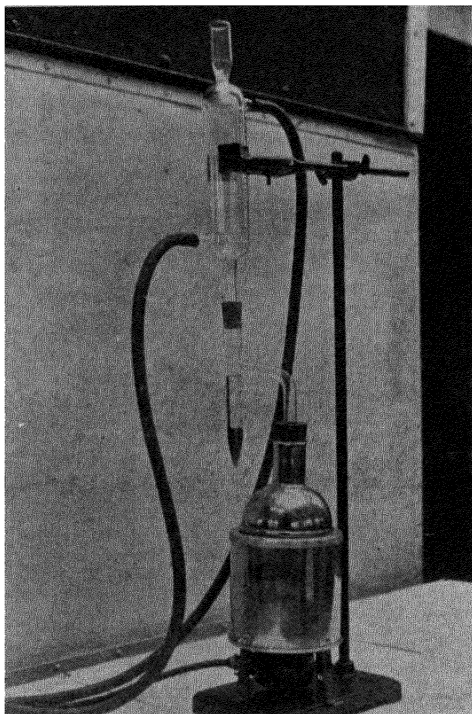


Fig. 4.—ESTIMATION OF WATER.

The sample is heated in a glass or copper flask with gasoline of specified properties. The water collects in the graduated measuring trap attached to the condenser. In the photograph the water layer has been coloured so as to emphasise the separation between the water and gasoline layers.

viscous products.

The Temperature Must be Carefully Controlled.

During the test the oil temperature must not vary to any appreciable extent and it may be necessary, especially during a test of long duration, to apply heat to the outer bath by means of a bunsen burner, the heating liquid being stirred by means of the agitator. A variation of as little as 0.5°F. from the test temperature may cause quite an appreciable error in the viscosity figures obtained.

Calorific Value.

The calorific value of gas oil or fuel oil is usually determined by the "bomb method," various types of

bomb calorimeter being in use in different laboratories. For a full description of the method used, and the calculation of the calorific value, see page 133.

Sulphur Content.

As in the case of calorific value, it is usual to determine the sulphur content in a bomb, although other methods have been proposed and are actually in use. Particular care should be directed to the lead gaskets of the bomb, since these are liable to form lead sulphate if any appreciable area is exposed. The ignition wire should be of fine platinum and all the reagents used should be sulphur-free. If this is not the case a blank test is made, so that the results of the test on the sample can be suitably corrected.

Not more than 1 gm. of oil is used for the test, and 10 c.c. of distilled water is placed in the bomb, which is charged with oxygen to at least 25 atmospheres and is

immersed in cold water before firing. After firing, the bomb is left in the water for ten minutes to allow absorption of the oxides of sulphur by the water, and the gas is then slowly released into the air. The bomb is emptied into a beaker and the cover and all the internal parts are washed out with distilled water. After filtration the washings are acidified with hydrochloric acid and boiled after the addition of a little sodium peroxide, the sulphur then being estimated gravimetrically as barium sulphate.

Water Content (I.P.T. Method F.O. 14).

The water content of petroleum products is estimated by distillation with a gasoline of specified properties in the Dean and Stark type of apparatus, using either gas or electric heating. The principle of the method has already been described on page 117 under the heading of "The Toluene Distillation Process," although for petroleum products the use of a special gasoline instead of toluene is specified. The complete apparatus, electrically heated, is depicted in Fig. 4.

The gasoline used for the water estimation test must have the following distillation characteristics:—

5 per cent.
distilling at a
temperature
not below 90°
C., not above
100° C.

90 per cent.
distilling at a
temperature
not above 205°
C.

Pour Test.

The pour test is described later in this article under the heading of "Lubricating oil"; it is sufficient to detail here the special precautions which must be taken when testing fuel oil samples. In

cases where it is known that a fuel oil sample has been heated to a temperature exceeding 115° F. during the preceding 24 hours, or where the history of the sample in this respect is unknown, the sample must be kept in the laboratory for 24 hours before testing. The result obtained is reported as the upper (maximum) pour point. A further portion of the sample is heated, with stirring, to a temperature of 220° F., and after pouring into the test jar and cooling to 90° F., the test is carried out in the manner to be described later. The result obtained is reported as the lower (minimum) pour point.

Ash.

The ash of gas oils or fuel oils is determined by igniting a suitable quantity of sample in a porcelain or silica dish or crucible over a small flame. After burning ceases the dish or crucible is heated more strongly (but at the lowest temperature necessary to effect complete removal of carbonaceous matter produced during the preliminary heating) until its weight is constant. Care should be taken to ensure that the temperature is not sufficiently

high to fuse the ash or to volatilise any chlorides which may be present. The amount of sample taken for the test depends on the amount of ash obtained, this varying from a negligible amount with distillate gas oils up to say 0.20 per cent. for heavy residual fuel oils.



Fig. 5.—POUR POINT TEST.

The oil is cooled under specified conditions until it ceases to move when the test jar is held horizontally for five seconds. In the photograph the operator has cooled down the oil to the "solid point." The test jar on the right of the photograph shows a second sample ready to be tested for pour point. Two jars on the left show samples subjected to the "cloud test," one before testing, the other one after testing. Reference should be made to the original I.P.T. method for details of the "cloud test."

Lubricating Oils.

The following tests are normally carried out on samples of mineral lubricating oil:

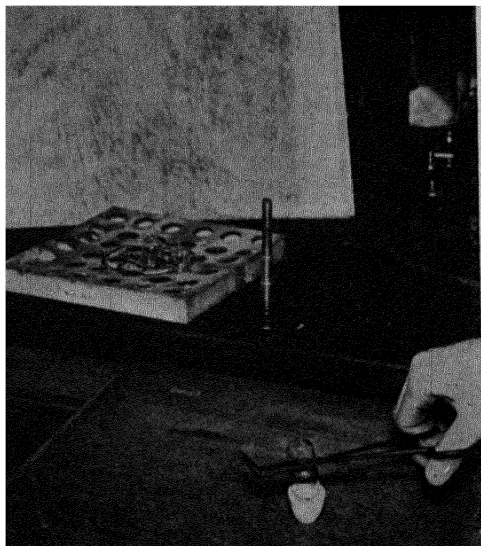


Fig. 6.—RAMSBOTTOM CARBON RESIDUE TEST (1).

The oil is heated in a small glass bulb in an iron sheath immersed in a bath of molten lead. One of the methods of filling the bulb is indicated in the photograph.

- (1) Specific gravity ;
- (2) Colour ,
- (3) Flash point ;
- (4) Viscosity ;
- (5) Pour test ;
- (6) Carbon residue.

Additional tests are made on compounded oils (i.e., lubricating oils containing fatty oils) and on such special products as transformer oils, turbine oils, etc., but these additional tests scarcely come within the scope of the present article. Details of such tests can be obtained from the I.P.T. Book of Standard Methods, or from the appropriate British Standard Specification.

Specific Gravity.

The remarks under the heading of "Gas Oils and Fuel Oils" are applicable also to lubricating oil. The hydrometer method is used whenever possible, although with the very viscous lubricating oils it may be necessary to fall back on the specific gravity bottle method.

Colour.

There is no generally accepted method for checking the colour of lubricating oil.

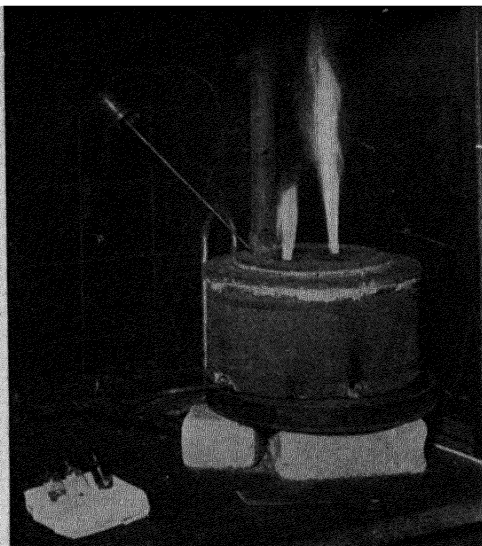


Fig. 7.—RAMSBOTTOM CARBON RESIDUE TEST (2).

The temperature of the bath must be controlled by means of a pyrometer and the bulb is left in the bath for ten minutes after fuming has ceased. The bulbs in the photograph show respectively a bulb ready for test, an empty bulb, and a bulb which has been through the test.

In America the Union Colorimeter is used for the purpose, and many chemists in this country employ the method also. In brief, the method is similar in principle to the Lovibond method (described under "Gasoline"), the sample being viewed through a test jar of 33 mm. diameter and compared with glass colour standards, numbered 1 to 8 (with intermediate standards). Alternatively, the Lovibond apparatus may be used, when the 18-in. cell used for gasoline or kerosene testing is replaced by a 1-in., $\frac{1}{2}$ -in., $\frac{1}{4}$ -in. or $\frac{1}{8}$ -in. test cell according to the depth of colour of the sample. The colour is matched in the usual way by means of standard glasses and, as a rule, it is necessary to use glasses of both the 510 (yellow) and 200 (red) series to get a satisfactory match.

POUR TEST (A.S.T.M. METHOD D. 97-34).

Definition and Significance of the Test.

The pour point is the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under definite prescribed conditions. The pour point gives an indication of the temperature below which it may not be

possible to pour or remove an oil from its container, or below which it might be unsafe to use the oil in gravity lubricating systems. No single test could be devised which would indicate positively the performance of an oil under service conditions, since the tendency to flow is considerably affected by such factors as the force or head exerted on the oil and the nature of its physical structure when solidified.

The Apparatus.

The test is carried out in a clear glass test jar as shown in Fig. 5, the jar containing the test sample being placed in a glass or metal jacket, with a cork-ring gasket and a cork disc to prevent the test jar from touching the jacket. The thermometer is placed centrally in the test jar, with its bulb just below the surface of the oil (note the test jar on the right of the photograph). The freezing mixture used for the test is chosen according to the pour test of the sample, and for oils of very low pour test it may be necessary to use a mixture of solid carbon dioxide and gasoline.

The Method.

The sample is poured into the test jar to a depth of 2-2½ in., and the thermometer placed in position. After heating the sample to 115° F. (in a bath of temperature not exceeding 118° F.) and allowing it to cool to 90° F. the jar is placed in its jacket and the latter is put into the cooling bath. At each thermometer reading which is a multiple of 5° F., the test jar is removed from the jacket and tilted sufficiently to ascertain whether there is any movement of the oil. The procedure is repeated for every 5° F. drop in temperature until a point is reached at which the oil does not move when the jar is held horizontally for exactly 5 seconds. The pour point is the temperature 5° F. above this solid point (i.e., the last temperature at which the oil was observed to move).

Flash Point.

The flash point of lubricating oils is determined by the Pensky - Martens Method, in the same way as for kerosene and fuel oil. The thermometer used is the "high-range" type, and applications of the test flame are made at every multiple of 5° F. instead of every 2° F., as when using the "low range" thermometer.

Viscosity.

The Redwood No. 1 instrument is employed for checking the viscosity of lubricating oils, the method being identical with that already described in this article. Tests are normally made at temperatures of 70° F., 140° F., and 200° F., although for more viscous oils tests may be made at 212° F. or 250° F.

Carbon Residue.

The standard method for determining the carbon residue is the Ramsbottom method, the oil being heated in a glass bulb of the type shown in Figs. 6 and 7. This bulb is a sliding fit in an iron tube or sheath which is maintained at a temperature of 550° C. in a bath of molten lead, the temperature being controlled by a pyrometer. About 4 gm. of oil is introduced into the glass bulb by inserting a glass capillary, suitably bent, and applying suction whilst the end of the bulb is immersed in the oil. Alternatively, the end of the bulb is dipped in the oil and heat applied to the bottom of the bulb by means of a small flame. The air expelled is replaced by oil when the bulb is allowed to cool down again. The bulb containing a weighed amount of oil is placed in the iron sheath and allowed to remain for 10 minutes after fuming has ceased. It is weighed when cool, the amount of residue in the bulb being reported as the "carbon residue" and calculated as a percentage on the weight of the original oil.

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ERRATA

- Page 18, col. 2, line 32. For "oxygen" read "nitrogen."
- Page 18, col. 2, line 33. For "nitrogen" read "oxygen."
- Page 20, col. 1, 18 lines from foot. For "ammonia" read "ammonium."
- Page 20, col. 2, 21 lines from foot. Delete "with unidirectional current."
- Page 20, col. 2, 6 lines from foot. Insert "see page 67" after "photograph."
- Page 36, col. 2, line 4. Delete "to produce poorer quality sugar."
- Page 49, col. 2, last line. Delete "To wax the coating."
- Page 116, col. 2, line 18. For "Hygrometer" read "hydrometer."
- Page 129, col. 2, line 31. Insert "dilute sulphuric" before "acid."
- Page 136, col. 1, line 18. For "အဝတ်" read "အဝတ်စုံ."
- Page 176, col. 2, line 4. Delete "c.c."
- Page 265, col. 1, line 21. For "chlorine" read "chloride."
- Page 280, col. 2, line 33. For "Tetlock" read "Tatlock."
- Page 398, col. 2, line 20. For " Na_2SiO_2 " read " Na_2SiO_3 ."
- Page 412, col. 2, line 33. For " Fe_3C " read " Fe_3C ."
- Page 416, col. 1, line 39. For "100 c.c." read "200 c.c."
- Page 438. Fig. 9. For "Polsenke" read "Kirschner."
- Page 443, col. 2, 12 lines from foot. For "with" read "within."
- Page 474, col. 1, 6 lines from foot. For "cooling" read "boiling."
- Page 482, col. 1, line 6. For "30240" read "12870."
- Page 482, col. 1, line 7. For "g/sq. metre" read "lbs. D.C. 480."
- Page 493, col. 1. Delete sketch showing chemical structure of cocaine. After "formula" insert "shown at the bottom of this column."
- Page 546, col. 1. Definition 4 applies to Grade A Pasteurised Milk only. In the case of Pasteurised milk the definition should be "a milk heat-treated as above containing not more than 100,000 bacteria per c.c."
- Page 554, Fig. 11. For "20 c.c." read "25 c.c."
- Page 621, col. 2, line 15. For "nitrate" read "nitrite."
- Page 633, Figs. 9 and 10. For "Aphanizo Messon" read "Aphanizomenon."
- Page 718, Fig. 1. Caption should read "Flow sheet showing production of various synthetic resins."
- Page 804, col. 1, 2 lines from foot. For "bromide" read "bromine."
- Page 943, col. 1, line 26. For "iodine" read "iodide."
- Page 950, Fig. 6, line 5. For "minute" read "second."
- Page 1010. In diagram read "A" for "B" and "B" for "A."
- Page 1137, Fig. 8. Insert "The residue in" in front of "The."
- Page 1268, col. 1, line 2. For "or" read "on."
- Page 1273, col. 2, line 25. For "nitrates" read "nitrites."
- Page 1312, col. 1, 10 lines from foot. For " $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ " read " $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$."

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